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MEASUREMENT OF VOLATILE CHEMICAL EMISSIONS FROM WASTEWATER BASINS

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16. ABSTRACT

The objective of this project was to measure the rate at which selected volatile organic carbon (VOC) compounds are being emitted to air from wastewater teatment basins of the pulp and paper industry. The emission rates of methanol, acetone and acetaldehyde were measured and the total hydrocarbon (FID) emission was quantified. Intermediate objectives were: develop a method of trapping , concentrating and analyzing low molecular weight volatiles in the presence of excess water vapor; develop turbulent transport theory using VOC concentrations and micrometeorology to determine flux rate from aerated stabilization basins.

A unique cryogenic sampling, concentration, and detection technique was developed along with a general protocol for flux determination called the concentration profile (CP) technique. The CP apparatus was conceived, designed and used in the field for flux determinations.

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FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment and even our health often require that new and increasingly more efficient pollutant monitoring and emission assessment methods be developed. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report documents a recently completed project. Its purpose was to develop a method of field measurement to quantify the emission flux rate of selected volatile organic chemicals from wastewater treatment lagoons. A method has been developed and used to measure the flux rates of methanol, acetone and total hydrocarbon from the surfaces of aerated stabilization basins of the pulp and paper industry. The methodology developed should be an important contribution in developing air monitoring techniques. The information contained in this report can also serve as a basis for future work. For further information, contact the Food and Wood Products Branch, IERL, Cincinnati, Ohio.

ABSTRACT

The objective of this project was to measure the rate at which selected volatile organic carbon (VOC) compounds are being emitted to air from wastewater treatment basins of the pulp and paper industry. The emission rates of methanol, acetone and acetaldehyde were measured and the total hydrocarbon (FID) emission was quantified. Intermediate objectives were: develop a method of trapping, concentrating and analyzing low molecular weight volatiles in the presence of excess water vapor; develop turbulent transport theory using VOC concentrations and micrometeorology to determine flux rate from water surfaces; and develop a mathematical model to predict emission rates from aerated stabilization basins.

A unique cryogenic sampling, concentration and detection technique was developed along with a general protocol for flux determination called the concentration profile (CP) technique. The CP apparatus was conceived, designed and used in the field for flux determinations.

The CP protocol calls for the measurement of chemical concentration, wind speed and temperature as a function of height above the water surface. All sampling is done within a height of two meters. The air space above the water surfaces of four pulp and paper wastewater treatment basins was sampled. Ranges of the average flux rates for the basins were: methanol, 1.4 to 3.8 $ng/cm^2 \cdot sec$ (11 to 29 lbs/acre·day); acetone, .028 to 0.10 $ng/cm^2 \cdot sec$ (.22 to 0.77lbs/acre·day); and total hydrocarbon (FID), 3.0 to 4.3$ng/cm^2 \cdot sec$ (23 to 33 lbs/acre·day). Acetaldehyde was detected, but at extremely low concentration.

The mathematical model was used with methanol and the predicted flux rate for the range of field conditions was 0.37 to 5.9 $ng/cm^2 \cdot sec$ (2.8 to 45

lbs/acre·day). The model results suggest that the dominant parameters that influence the volatilization of methanol are: concentration of methanol in the water, water temperature, and wind speed. It appears that the methanol volatilization is gas-phase controlled. Only methanol data was used with the predictive model.

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SECTION 1

INTRODUCTION

The overall objective of this work was to determine the magnitude of the flux rate of organic compounds that are emitted into the air from selected wastewater treatment facilities for the pulp and paper industry. In order to make these measurements, it was necessary to develop a field sampling methodology, hereafter called the concentration profile (CP) technique, and laboratory analysis methodology to trap and measure low molecular weight, volatile organics in air.

Various organizations, including the chemical process industries, and federal and state agencies, are concerned about aspects of air emissions from wastewater treatment basins. In some cases, efforts are aimed at odor control. In other cases, there is concern for the emission of hazardous substances, which originate from surface impoundments, into the air. There is also a general concern for emission of vapor phase organics and inorganics from wastewater treatment basins. The placement of organic compounds (non-sulfurous) in these basins gives rise to vapor phase organic (non-methane) emissions that increase the quantity of hydrocarbons in the nearby air mass. In this regard, attention has been focused on wastewater treatment basins as a source of potentially hazardous trace contaminants to air.

As a result of interest generated during an EPA demonstration project (McAlister et al., 1971) with Georgia Kraft Company that evaluated the effectiveness of cooling towers as a combined wastewater cooling, biotreatment and stripping operation, research was initiated at the University of Arkansas to develop an apparatus to quantify the air-strippable organic fraction in

industrial wastewater (Thibodeaux, 1974). A mathematical simulation of air-stripping and natural desorption (Thibodeaux and Parker, 1976) from aerated stabilization basins suggested that a significant quantity of volatile organic material is escaping treatment by the air route. Further studies of raw wastewaters representing a broad spectrum of industrial operations including the wood products industry suggested that a significant fraction of the discharged organic material was volatile and easily stripped by air (Thibodeaux and Millican, 1977). Gas chromatograph/mass spectrometer analysis of organic compounds in treated Kraft mill wastewater indicate that many of these compounds are known volatile chemicals, (Keith, 1976).

There is no question that quantities of chemicals are escaping through the air-water interface of wastewater treatment facilities. The question is how much of what chemicals are desorbing. Due to various sinks for chemicals in the facilities which include water seepage, biochemical oxidation, adsorption upon the sediments and particulate matter, etc., a realistic approach to quantifying the flux to the air is to perform measurements in the air boundary layer immediately above the water surface.

This report contains the following:

a) a development of turbulent transport theory for chemical flux measurement from water surfaces (see Section 3);

b) the methodology for performing micrometeorological and chemical measurements used in the concentration profile (CP) technique (see Section 4);

c) field results of the emission rates of methanol, acetone, acetaldehyde, and total hydrocarbon (GC/FID) from four pulp and paper wastewater basins (see Section 5);

d) a model for predicting chemical desorption rates (see Section 6b).

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Volatile chemicals in the wastewater are emitted into the overlying air boundary layer. Air samples in a two-meter region above the water surface had quantities of methanol, acetone and total hydrocarbon in levels much higher than the background. Concentrations in the layer decreased significantly with height above the water.

2. A field sampling method and associated apparatus referred to as the concentration profile technique, was developed and tested. The technique is based on obtaining samples of air, wind velocity and temperature in a two meter boundary layer region above the water surface. The flux rates of methanol, acetone and total hydrocarbon originating in aerated stabilization basins were measured during field tests of the technique. Flux rates were roughly 16, 0.46 and 23 pounds per acre per day for these chemicals respectively.

3. A mathematical model was presented to predict the emission rate of volatile chemicals from surface impoundments. Field flux measurements for methanol was used to verify aspects of the mathematical model. Intrepretation of the model results suggests that the emission of methanol increases with increases in concentration of the species in water, wind speed, and water temperature.

RECOMMENDATIONS

1. The concentration profile (CP) technique should be tested further to determine the degree of reproducibility of the measurements. This can be done best by exhaustive sampling on a single lagoon at one location of the surface.

2. The CP technique should be further tested in measuring emissions

from all types of surface impoundments including: wastewater treatment basins of other industries, sludge basins, solvent dump pits, land application of sludges, land application of wastewater, landfills, etc. In this regard it will be necessary to develop and test alternative trapping and chemical analysis techniques.

3. Other flux measuring techniques should be developed for those impoundments for which the CP method is not applicable because of up-wind disturbances, short fetch, low or no wind, and other reasons listed in Section 5 (p. 57).

4. The CP technique should be used to measure the emission rate of a low solubility, liquid phase controlled species such as benzene or toluene. This should provide the necessary field data for final verification of the predictive model.

SECTION 3

THEORY OF THE CONCENTRATION PROFILE TECHNIQUE

a. GOALS, HIGHLIGHTS AND FINAL WORKING EQUATIONS

Presented in this sub-section are the working equations and some details of the concentration-profile theory. These working equations are used to calculate the air emissions from the sampling data. They are from the detailed theoretical development in the following sub-section, as they appear (and are numbered) in that development. Those readers seeking details of the micrometerology and transport science basis of the working equations should refer to that sub-section. The presentation below is more user-orientated and should be sufficient background for calculating emissions.

Field measurements of the concentration of the chemical in air, $\overline{\rho}_{A1}$, wind speed, $\overline{v}_x$, and temperature $\overline{T}_1$, within the turbulent boundary no more than two meters above the water surface, need be made. Six observations of each variable, distributed in a logarithmic fashion from the water surface, taken well downsind of any wind velocity disturbances, should be made. Based on these measurements, Equation 24 is used to determine the vertical flux of the chemical (i.e., species B) from the water surface. Equation 24 is:

$$n_B = - \mathscr{D}_{B1} / \mathscr{D}_{A1})^{2/3} \, S_v S_\rho k^2 / \phi_m^2 \, Sc_{A1}^{(t)} \qquad (24)$$

$k = 0.4$ (von Karman constant).

Since the air sampling is done so close to the water surface, only the vertical flux is needed to assess the emission rate from the water surface.

The flux rate, n_B, is in grams of species B per second per square centimeter of water surface ($g/s \cdot cm^2$). S_ρ is the slope of a line from a graphical

plot (or linear regression, computer generated) of $\bar{\rho}_{A1}$ (g/cm^3) vs. ln y, where y is the sample height above the water surface in cm. Figure 7 is an example of such a concentration profile. For flux of chemical B from the water surface, the slope should be a negative number of units g/cm^3. S_v is the slope of a line from a similar relation between v_x (cm/s) vs. ln y. This slope should be a positive number and have units of cm/s. The combination of the units of S_ρ and S_v is the units of flux.

Only if the air boundary layer is neutral should the concentration and velocity vs. ln-height profiles be linear over the entire range of the six observation heights. The profiles may be non-linear under stable and unstable micrometeorological conditions and display some curvature. In this case, the slopes of tangent lines drawn to the profiles in the boundary layer region nearest to the water surface should be used for S_ρ and S_v.

The stability category of the air boundary layer is obtained by determining the Richardson Number. The Richardson Number (i.e., Ri) is computed from temperatures and wind velocities in the boundary layer by Equation 18. The equation is:

$$Ri \simeq \frac{g}{\bar{T}_1} \frac{(\bar{T}_{12} - \bar{T}_{11})(y_2 - y_1)}{(\bar{v}_{x2} - \bar{v}_{x1})^2} \qquad (18)$$

g is the gravitational acceleration constant (i.e., 980.7 cm/s^2). $\bar{T}_{12}$ and $\bar{T}_{11}$ are average dry bulb air temperatures at sample heights y_2 and y_1 above the water surface, respectively. $\bar{v}_{x2}$ and $\bar{v}_{x1}$ are average wind speed at sample heights y_2 and y_1, respectively. The sample heights (i.e., y_1 and y_2) used in Equation 18 for the Ri determination should be in the same region of the boundary as the S_ρ and S_v values used. The arithmetic average, $\bar{T}_{12}$ and $\bar{T}_{11}$, is usually sufficient for estimating T_1. Ri is dimensionless. A negative value

of Ri results if the air is unstable. If Ri = 0, the air is neutral and if Ri > 0, the air is stable.

The Richardson number provides a means of assessing the low-wind speed limitation of Equation 24 for the flux determination and the application of the stability correction factor $(\phi_m^2 \, Sc_{A1}^{(t)})^{-1}$. If conditions are stable, Equation 24 should be used only for $|Ri| \leq 1.0$. If conditions are unstable, Equation 24 should be used only for $|Ri| \leq 4.0$. The correction factor is then estimated by:

$$(\phi_m^2 \, Sc_{A1}^{(t)})^{-1} = (1 \pm 50 \, Ri)^{\pm 1/2} \qquad (25)$$

where -50 and +½ apply for unstable conditions and +50 and -½ apply for stable conditions. The correction factor is unity for neutral conditions.

Equation 25 is an empirical correlation factor that corrects the neutral condition, concentration profile flux estimate for water vapor (i.e., $n_A = -S_\rho S_v k^2$) to the actual water vapor flux from ground sources under non-neutral conditions. This water vapor flux calibration factor and associated $|Ri|$ values places limitations on the use of Equation 24 for flux estimates since it has not been verified outside the given Ri range. The 2/3 power ratio of the molecular diffusivities of the chemical of interest to that of water vapor (i.e., $\{\mathcal{D}_{B1}/\mathcal{D}_{A1}\}^{2/3}$) corrects the equation for the chemical in which the flux is desired. Both the correction factor and the diffusivity ratio are dimensionless.

The three equations presented above are the working formulas of the concentration profile method. Appendix D contains a sample calculation of the flux rate illustrating the use of the above three equations. The next section presents a detailed derivation and justification of the equations.

b. MODEL DEVELOPMENT

One prime objective of the science of micrometeorology is to study the atmospheric boundary layer to obtain tractable expressions for the fluxes of heat, momentum, water vapor and other atmospheric constituents. The complexity of turbulence is such that so far only semi-empirical relationships have been developed, and micrometeorologists continue to work on refinements. However, from an engineering standpoint the science can be used in its present form, within proper limitations, to obtain chemical flux estimates from surface impoundments.

This sub-section presents the technical background, including the micrometeorology, of the so-called concentration profile technique for estimating chemical flux rates from surface impoundments. The document presents and discusses the limitation of the analytical model, and since the technique employs field observations, the document also provides some guidelines for proper sampling methodology.

Boundary Layer

In air flow over a large region, the effects of the earth's frictional forces induce the creation of a boundary layer. The boundary layer extends, by definition, to the height at which velocity is about 99% of that in the free air above. The size of the atmospheric boundary layer depends, of course, on the wind speed and on the type of terrain, but it is usually of the order of 1000 m. Beyond this layer is an environment free of viscous or turbulent shear called the free layer. In the absence of shear stresses, the motion of the free layer is strongly governed by the rotation of the earth and consequently is given the name of geostrophic layer where the motion is called geostrophic.

Below the free layer is the outer layer or the Ekman layer, which is

influenced by Coriolis, pressure and Reynolds stresses. Near the surface in a layer a few meters high the mean velocities are small and, consequently, the inertia and the Coriolis forces, which depend on velocity, are negligible compared to the shear forces (viscous and Reynolds), which appear to be constant in this inner layer. Each mountain, building, levee or surface feature of varying roughness or height has its effect on the air stream passing over it, and a local boundary layer equilibrated to each surface develops within the inner layer. FIGURE 1 illustrates the development of a local boundary layer above a surface impoundment. It is in this local boundary layer of the inner atmospheric layer that micrometeorological techniques can be utilized to obtain emission flux rates from surface sources.

The Phenomenological Flux Equations

The flux rate of chemical from the water surface in the re-established boundary layer region is:

$$n_A = - (\mathcal{D}_{A1} + \mathcal{D}_{A1}^{(t)}) \, d\bar{\rho}_{A1}/dy \qquad (1)$$

where: n_A is the flux rate in $g/cm^2.s$

$\mathcal{D}_{A1}$ is the molecular diffusibity in cm^2/s

$\mathcal{D}_{A1}^{(t)}$ is the turbulent diffusivity in cm^2/s

$\bar{\rho}_{A1}$ is time-smoothed average atmospheric concentration of A in g/cm^3

y is distance from the water surface in cm.

With expressions for the gradient and diffusibities and field measurements of concentration and micrometeorology Equation 1, in principle, can be used to estimate the flux rate. Similar phenomenological expressions apply for the transport of momentum:

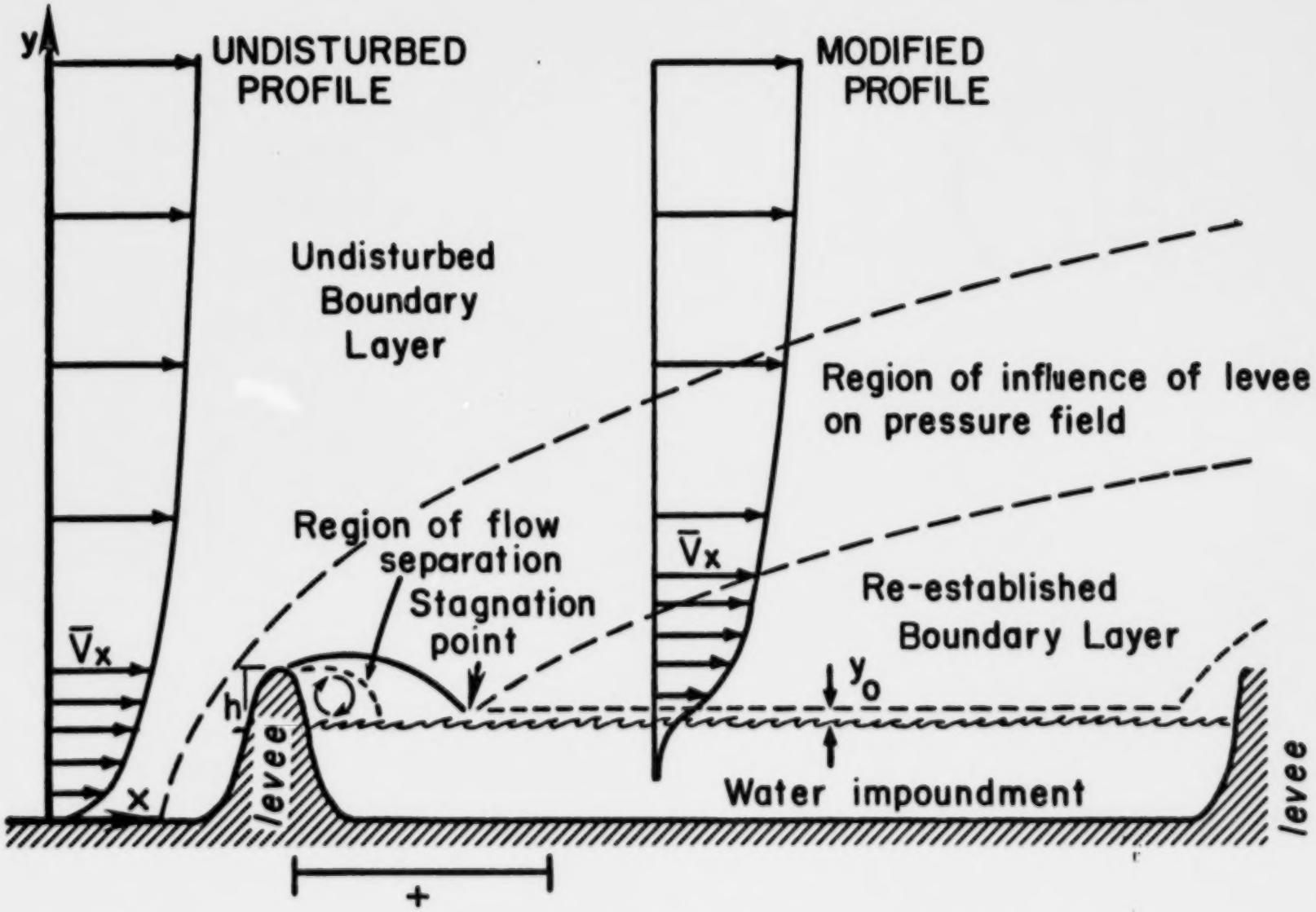


FIGURE I. BOUNDARY LAYERS ABOVE A SURFACE IMPOUNDMENT

$$\tau = \rho_1(\nu_1 + \nu_1^{(t)})\ d\bar{v}_x/dy \qquad (2)$$

and sensible heat:

$$q = -\rho_1 c_p(\alpha_1 + \alpha_1^{(t)})\ d\bar{T}_1/dy \qquad (3)$$

in the re-established boundary layer region,

where: τ is the shear stress in the surface layer in $g/cm \cdot s^2$

ρ_1 is air density in g/cm^3

ν_1 is kinematic viscosity of air in cm^2/s

$\nu_1^{(t)}$ is turbulent viscosity in cm^2/s

$\bar{V}_x$ is the time-smoothed x-component of wind velocity in cm/s

q is the sensible heat flux from the water in $J/cm^2 \cdot s$

c_p is specific heat of air in $J/g \cdot K$

α_1 is the thermal diffusivity in cm^2/s

$\alpha_1^{(t)}$ is the turbulent thermal diffusivity in cm^2/s

$\bar{T}_1$ the time-smoothed air temperature in K.

The Logarithmic Layer

The inner or surface layer is usually defined as the logarithmic layer and is the lowest part of the boundary layer where fluxes may be considered independent of height. This is approximately the case in the lowest 10 to 20 meters. In this layer, the interaction with the water surface is very strong and adjustments to the surface conditions are relatively rapid. A quasi-steady state, with respect to the build-up of the surface boundary layer may, therefore, often be assumed. Employing Prandtl's mixing-length hypothesis and simple dimensional analysis, Sutton (1953) developed the following semi-

empirical expression for the turbulent viscosity:

$$\nu_1^{(t)} = kv_* y \tag{4}$$

which, on integration with $\nu^{(t)} >> \nu$ gives the well-known logarithmic wind profile. v_* is the surface friction velocity (i.e., $v_* \equiv \sqrt{\tau/\rho_1}$). For motion near smooth pipe surfaces, Nikuradse found that the logarithmic velocity profile was:

$$\bar{v}_x = \frac{v_*}{k} \ln\left(\frac{v_* y}{\nu_1}\right) + 5.5 \tag{5}$$

with $k = 0.4$.

The logarithmic profile applies only to the pure turbulent region of the surface boundary layer where the Reynolds stresses predominate. It is a semi-theoretical equation in that the von Karman constant, k, and one other constant must be determined by experiment. Their precise physical meaning is not fully understood. Schlichting (1979) presented evidence that the logarithmic profile also applies in the turbulent region above a smooth flat plate. The appropriate equation is:

$$v_\infty - \bar{v}_x = \frac{v_*}{k} \ln(\delta/y) \tag{6}$$

where: v_∞ = is the free-stream velocity in cm/s

δ = is the boundary-layer thickness of the plate in cm.

While the earth's surface is rarely aerodynamically smooth, it does occur, notably with light winds over water, snow, ice surfaces and salt flats. Water surfaces are, in general, quite smooth even in the presence of substantial

wind-driven waves.

In the fully-rough regime, the influence of viscosity is negligible and the logarithmic profile is usually written in the form:

$$\bar{v}_x = \frac{v_*}{k} \ln (y/y_0) \qquad y >> y_0 \qquad (7)$$

where: y_0 = is a constant of integration known as the roughness length (in cm), which must be related in some way to the size of the protuberances.

In the case of either smooth or rough flow, the respective profile equations, Eq. (5) and Eq. (7), are for the turbulent region of the boundary layer. From Eqns. (2) and (4), when $kv_* y_0 << \nu_1$, the flow at the surface is entirely determined by viscous shear and turbulent shear is negligible. This condition is called "aerodynamic smooth flow". In general terms, a surface is called aerodynamically smooth if the protuberances are sufficiently small to allow the formation of a laminar sublayer, in which they are entirely submerged. An aerodynamically rough surface is one in which the irregularities are large enough to prevent the formation of any such layer, so that the motion is turbulent down to the surface itself. Since the depth of the laminar sublayer depends on the magnitude of the Reynolds number, the classification of a surface according to the above definitions thus involves not only the geometric characteristics of the boundary but also the magnitude of the mean velocity, so that a surface which is "smooth" at low velocities may become "rough" as the mean velocity increases. In practice, since the laminar sublayer is always very shallow, a surface which is aerodynamically smooth at moderate Reynolds numbers must also be fairly smooth in the everyday sense of the word. See Sutton (1953) for other discussions concerning aerodynamically smooth flow.

Nikuradse carried out extensive wind tunnel experiments in order to define the transition from smooth to rough flow. He found that for

$$v_* y_0/\nu < 0.13 \tag{8}$$

the flow is smooth and that for

$$v_* y_0/\nu > 2.5 \tag{9}$$

the flow is fully rough. A transition regime exists in between those two values. The above has important consequences for micrometeorological air sampling in that it establishes, through y_0, a minimum height above which the flow is turbulent.

The logarithmic wind profile expression, Eq. (7), applies to natural surfaces such as soil, grass and water only under conditions of neutral or near neutral stability. The diabatic surface layer is different from the neutral surface layer because the turbulent structure is affected by the presence of a heat flux.

The Diabatic Case

Neutral or near neutral conditions exist only for short periods at sunrise and sunset or on overcast days when the air and soil is at or near the same temperature. When non-neutral conditions exist, the slope of the wind profile deviates significantly from the logarithmic ideal. Sutton (1953) illustrated the deviation graphically (on ln y vs. $\bar{v}_x$ coordinates) with concave downward relation for unstable conditions and concave upward for stable conditions.

Monin and Obukhov modified Equation 4 for use under all stability conditions by:

$$\nu_1^{(t)} = kv_* y/\phi_m \tag{10}$$

where: ϕ_m is a function of y/L

L (Obukhov scale length)in cm is given by:

$$L = -\rho_1 c_p v_*^3 T_1/kgq \tag{11}$$

where: g is gravitational acceleration 980.7 cm^2/s.

This length was conceived by Obukhov to be the height above the surface at which the mechanical energy production is equal to the buoyant energy production and serves as a characteristic height which determines the structure of the surface layer.

Businger (1973) correlated wind shear observations, ϕ_m, from micrometeorological measurements with dimensionless height, ζ, created from the Obukhov scale length. The observations fit the following analytical expressions quite well:

$$\phi_m = (1 - 16\zeta)^{-1/4} \qquad \text{for } \zeta < 0 \tag{12}$$

and

$$\phi_m = 1 + 4.7\zeta \qquad \text{for } \zeta \geq 0 \tag{13}$$

where: $\zeta \equiv y/L$.

These relations define the structure of the diabatic surface layer and in so doing provide a means of quantifying the velocity gradient under these conditions. He presented the following equation for describing the profiles under diabatic conditions:

$$\bar{v}_x = \frac{v_*}{k}\left(\ln \frac{y}{y_0} - \Psi\right) \tag{14}$$

where Ψ = is a complex function of ϕ_m. He further suggested a method of least-squares fitting of smoothed velocity and temperature profile observations whereby the heat flux rate from the surface can be obtained. Presumably, the mass flux can be determined in an analogous fashion.

In the unstable range, the Richardson number, Ri, is approximated by ζ, which makes the description of the surface layer rather simple. The Richardson number is an alternative means of obtaining a stability parameter. It is the ratio of consumption of turbulent energy by buoyancy forces divided by the rate of production of turbulent energy by wind shear and reduces to:

$$Ri \equiv (g/\bar{T}_1)(\partial \bar{T}_1/\partial y)/(\partial \bar{v}_x/\partial y)^2 \tag{15}$$

for the first few meters near the ground. Numerical values can be computed from observations of temperature and wind velocity profiles.

Several other investigators have developed diabatic correlations by relating ϕ_m directly to Ri. These efforts have been summarized by Rosenberg (1974) and include the work of Holzman, Panofsky, Lumley, Dyer, Hicks, Webb, Oke, Swainbank, Businger and Rider, and involve relations of the form

$$\phi_m = (1 \pm bRi)^{\pm 1/n} \tag{16}$$

where b and n are empirically determined constants and the sign relates to the stable or unstable case. TABLE I contains constants for various well-known correlations. The correlations have limited Ri applicability: stable, $|Ri| \leq 1.0$ and unstable $|Ri| \leq 4.0$.

TABLE 1

CONSTANTS FOR ϕ_m vs. Ri CORRELATIONS

Correlation Name	Stability Class	b	n
OKE	Stable	10	2
UCD*	Stable	16	3
KEYPS†	Stable	18	4
KEYPS	Stable	38	4
HOLZMAN	Unstable	-9	-2
KEYPS	Unstable	-18	-4
KEYPS	Unstable	-38	-4
UCD	Unstable	-16	-3

*University of California, Davis

†Several investigators, independent research

Modified Thornthwaite-Holzman Equation

In 1939, Thornthwaite and Holzman developed a gradient method for determining the flux of water vapor from land and water surfaces. Their procedure assumed $\mathcal{D}_{A1}^{(t)}/\nu_1^{(t)} = 1$ and was only reliable under near-adiabatic conditions. In the case we want to study, the transfer of a trace constituent to the atmosphere, it is advantageous to link it to the transfer of water vapor. Brooks and Pruitt (1965) developed and presented the modified Thornthwaite-Holzman Equation for water vapor flux above a crop surface:

$$n_A = \frac{k^2 (\bar{v}_{x2} - \bar{v}_{x1})(\bar{\rho}_{A12} - \bar{\rho}_{A11})}{\phi_m^2 \, Sc_{A1}^{(t)} \{\ln[(y_2 - d)/(y_2 - d)]\}^2} \qquad (17)$$

where: n_A is the flux rate of water in $g/cm^2 \cdot s$

$Sc_{Al}^{(t)}$ is the turbulent Schmidt number (i.e., $Sc_{Al}^{(t)} \equiv \nu_l^{(t)} / \mathscr{D}_{Al}^{(t)}$

d(cm) is the zero plane displacement for the crop which replaces y_0 for flat surfaces.

Equation (17) requires two observations of velocity, concentration and temperature at exactly the same heights and this somewhat limits its utility.

Temperatures are necessary to compute the Richardson number (Eq. (15)), which can be expressed in finite difference form:

$$Ri \simeq \frac{g}{\bar{T}_1} \frac{(\bar{T}_{12} - \bar{T}_{11})(y_2 - y_1)}{(\bar{v}_{x2} - \bar{v}_{x1})^2} \qquad (18)$$

where subscripts denote elevation points 1 and 2. Pruitt found that $Sc_{Al}^{(t)}$ was not unity but also related to Ri. Field results of eddy viscosity and turbulent diffusivity of water vapor are correlated with the following relationships:

$$Sc_{Al}^{(t)} = 1.13(1 + 95\ Ri)^{-0.11} \qquad (19)$$

for stable conditions with $|Ri| \leq 0.5$ and

$$Sc_{Al}^{(t)} = 1.13(1 - 60Ri)^{0.074} \qquad (20)$$

for unstable conditions with $|Ri| \leq 4.0$

In the case of several closely spaced sensors and samplers positioned at unequal distances from the surface in the lower two meters of the boundary layer, Eq. (17) is cumbersome to use for flux calculations. Relations involving profile in this region using up to six observations of concentration and velocity are more flexible. Equation (2) can be integrated with the use of Equation (1) to yield the velocity profile equation for neutral and non-neutral conditions:

$$\bar{v}_x = \frac{v_* \phi_m}{k} (\ln y - \ln y_0) \tag{21}$$

In a similar fashion Equation (1) can be integrated for trace constituent B with

$$\mathcal{D}_{B1}^{(t)} = (\mathcal{D}_{B1}/\mathcal{D}_{A1})^{2/3} \, kv_* y/\phi_m Sc_{A1}^{(t)} \tag{22}$$

where the molecular diffusivity ratio, $(\mathcal{D}_{B1}/\mathcal{D}_{A1})^{2/3}$, corrects turbulent diffusivity of water vapor for the chemical constituent of concern. Integration yields the concentration profile equation:

$$\bar{\rho}_{B1} = \rho_{B1}\Big|_{y_0} - \frac{n_B \phi_m Sc_{A1}^{(t)}}{(\mathcal{D}_{B1}/\mathcal{D}_{A1})^{2/3} \, kv_*} (\ln y - \ln y_0) \tag{23}$$

where: $\rho_{B1}\Big|_{y_0}$ is the concentration of species B at $y = y_0$. It should not be inferred that Equations (21) and (23) are linear throughout the two-meter sample zone.

Field observations of $\bar{v}_x$ and $\bar{\rho}_{B1}$ may be displayed graphically (or analytically), according to Equations (21) and (23), as $\bar{v}_x$ vs. ln y and ρ_{B1} vs. ln y to yield profiles. With the control of up to six observations of each variable, straight lines may be fitted (least squares or visually) to portions of or the entire profile. The slopes of the velocity profile line, S_v, in cm/s and the concentration profile line, S_ρ, in g/cm^3, can now be used to obtain an estimate of the flux rate of chemical B. Using the slope terms of the linear Equations (21) and (23) yields:

$$n_B = -(\mathcal{D}_{B1}/\mathcal{D}_{A1})^{2/3} S_v S_\rho k^2/\phi_m^2 \, Sc_{A1}^{(t)} \qquad (24)$$

Ri should be calculated in the same region that S_v and S_ρ were extracted. It should be noted that a construction of velocity and concentration profiles under diabatic and neutral conditions requires a knowledge of y_0 and $\rho_{B1}\big|_{y_0}$; however, the effect of these variables is not felt when only gradients are considered. In reality, Equation (24) is a more flexible version of the modified Thornthwaite-Holzman equation (i.e., Eq. (17)), and both employ gradients. S_ρ will be a negative number for the net loss of a trace constituent from a surface so that the flux is positive. If S_ρ is positive, then deposition at the water surface is indicated.

Limitations on Equation (24) or (17)--

It was noted early in this paper that the level of meteorological science for near-surface flux estimation rests in large part on a semi-empirical basis. This can be appreciated by a brief review of the reported measured values of k, the von Karman constant. Wind tunnel experiments suggest k = 0.4. Experiments in the atmosphere show a large scatter (i.e.,

0.33 to 0.41). Recent experiments by Businger yielded k = 0.35, which is almost in agreement with large Reynolds numbers in wind tunnels, 0.33. Values for tube flow range from 0.36 to 0.4. There is some evidence that the von Karman constant is not quite constant but varies and is smaller for rough surfaces than for smooth surfaces. Besides this variation, it is of no consequence which value is accepted since other empirical parameters or functions (i.e., ϕ_m and $Sc_{Al}^{(t)}$) are needed to complete the flux expression. These functions were apparently obtained with k = 0.4.

The diabatic velocity profile correction factor, ϕ_m, and the turbulent Schmidt number, $Sc_{Al}^{(t)}$, are available for limited Richardson numbers. The data on ϕ_m vs. Ri is rather exhaustive, but that for $Sc_{Al}^{(t)}$ is small and limited to observations on water vapor. The field data supporting these two empirical functions likely contain the highest degree of fluctuations and will cause a sizable range of uncertainty in flux computations. For example, under unstable conditions at Ri = -1.0, the product $\phi_m^2 Sc_{Al}^{(t)}$ ranges from 5 to 10 (Brooks and Pruitt, 1966). This will cause a factor of two variation in n_B. Brooks and Pruitt (1966) developed a correction factor that combines ϕ_m and $Sc_{Al}^{(t)}$:

$$(\phi_m^2 Sc_{Al}^{(t)})^{-1} = (1 \pm 50\ Ri)^{\pm 1/2} \qquad (25)$$

where -50 and +1/2 apply for unstable and +50 and -1/2 apply for the stable case.

With respect to slope determinations from concentration and velocity logarithmic profiles, S_ρ will likely contain more variation than S_v because of the difficulty of the atmospheric chemistry determinations at the low

level of the trace constituents normally encountered. However, with methanol we have obtained five profile slope observations from a surface impoundment with correlation coefficients of 0.964 or better. Long sample time and/or larger samples will minimize the uncertainty in S_ρ and S_v.

Molecular diffusivities are known with a relatively high degree of accuracy (i.e., $\pm$5%). The 2/3 power of this correction factor is borrowed from turbulent boundary layer evidence on flat plates.

Limitations on Methodology--

It is obvious from the technical development that the region of application must be within the turbulent region of the surface boundary layer. The turbulent portion is that region where $kv_*y >> \nu_1$, and sampling should not be done at or below this height. Equations (8) and (9) help define this height; however, y_0 values for typical surface conditions are small. Slade (1968) reported values (in centimeters) of 0.001 for smooth mud flats and ice, .005 for smooth sea, 0.3 for level desert, 0.1 for lawn to 1 cm high and 1.0 to 2.0 for lawn with grass to 5 cm. height. It appears that samples can be placed within a few inches of the water surface and still be well within the turbulent zone.

A horizontal uniform, two-dimensional surface is necessary for successful use of the theoretical model. There are many natural surfaces, including some surface impoundments, that cannot meet these conditions. According to Parmele et al. (1972), surface inhomogeneity not only affects $Sc_{Al}^{(t)}$, but also may create sampling problems in representative measurement of gradients. All micrometeorological techniques can be applied with confidence only when the site satisfies relatively demanding uniformity criteria. In cases for which uncertainties exist about the suitability of a specific site, surveys

to test the extent of horizontal homogeneity are usually of great value.

When sensors are elevated to obtain better spatial sampling and to obtain maximum possible vertical distances, the profile measurements of wind, temperature and vapor concentration are affected more and more by surfaces further upwind and less by the surface immediately below the sensor. At some point the measured profile gradients are not representative of the processes occurring on the reference surface. The fetch requirement is a measure of the minimum upwind distance of a site from a significantly different surface which is necessary for a representative measurement of the meteorological variables. Inhomogeneity influences fetch requirements in that height to fetch ratios (i.e., h:f) required should be 1:50 for "minor" discontinuities and at least 1:100 or 1:200 if the discontinuity is severe. It has been reported that these "ideal" fetch requirements are difficult if not impossible to satisfy under many field situations, particularly in regard to tall agricultural crops such as corn. These matters are of considerable importance; if insufficient fetch is available or if the site is inhomogeneous, local flux divergences might have an overwhelming effect.

SECTION 4

MATERIALS AND METHODS

a. FIELD SAMPLING PROCEDURES

Air hydrocarbon concentration samples, wind direction and velocity measurements, temperature measurements and water samples were taken at several points in each lagoon sampled. All measuring equipment was mounted on a barge for easy access to the different locations on the lagoon. All measurements and samples were taken at each sampling point on the lagoon within a six minute sampling period.

Air Concentration Measurements

Six samples were taken simultaneously at each sampling point on the lagoon. Sampling devices were mounted on a concentration mast and the mast was mounted on the front of the sampling barge as shown in FIGURE 2.

The concentration mast was an eight-foot vertical construction made of five-eights inch aluminum plate and one-inch iron pipe. The basic mast is shown in FIGURE 3. As shown, there are three uprights. On each of these is mounted two sampling devices. These devices are designed to slide easily up and down the upright but are fitted with clamps to hold them firmly in the desired position. Each sampling device holds a 300 ml. Dewar flask. Also fitted to the sampling devices are connections for the sampling tubes and a tube leading to the appropriate rotameters. The details of the sampling device are shown in FIGURE 4.

The bank of six rotameters was purchased from Matheson Gas Products. The rotameters were each fitted with a metering valve. The bank of rotameters shares a common outlet. Each rotameter tube can measure a flow of zero to

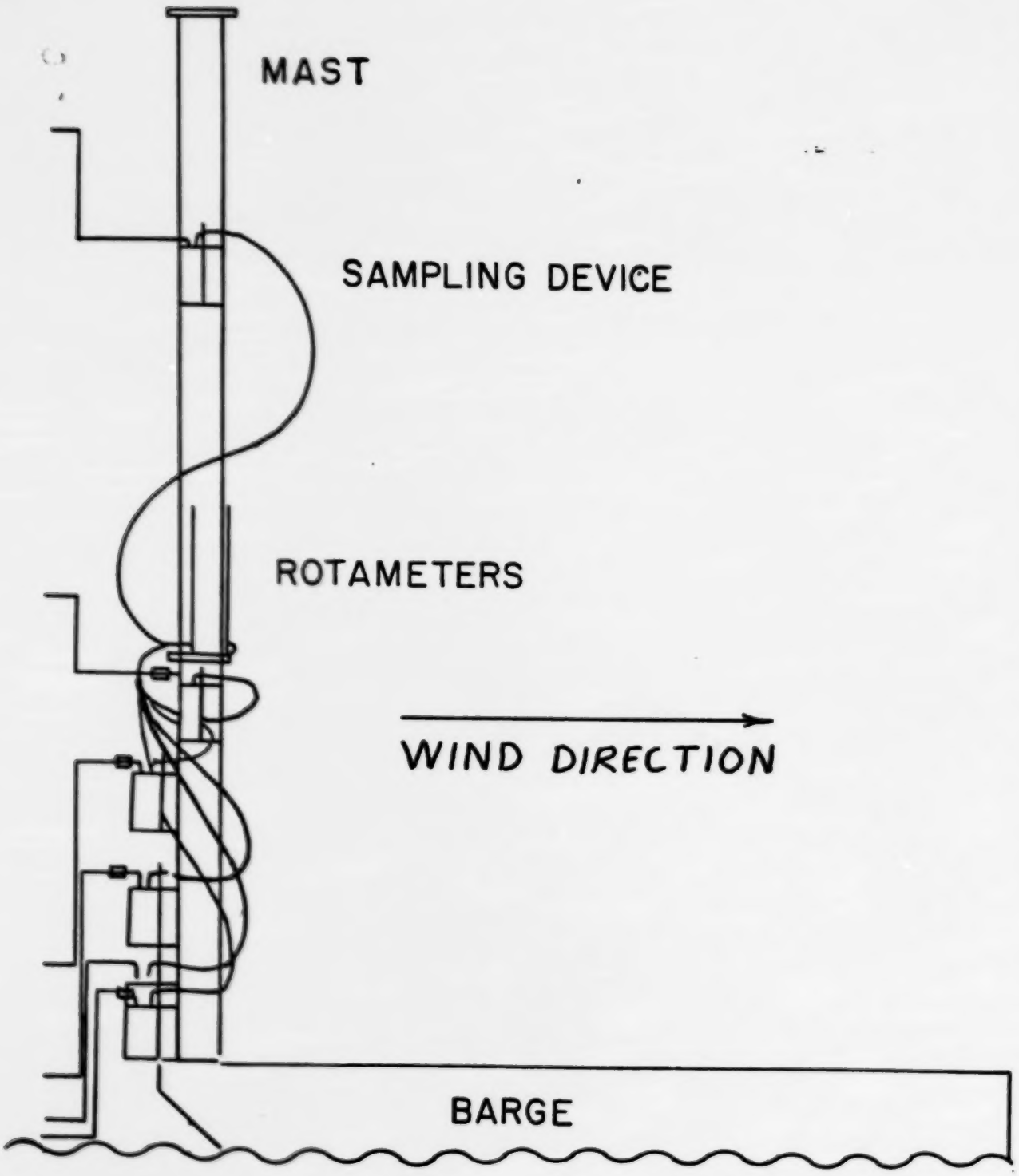


FIGURE 2. CONCENTRATION MAST IN PLACE ON BARGE

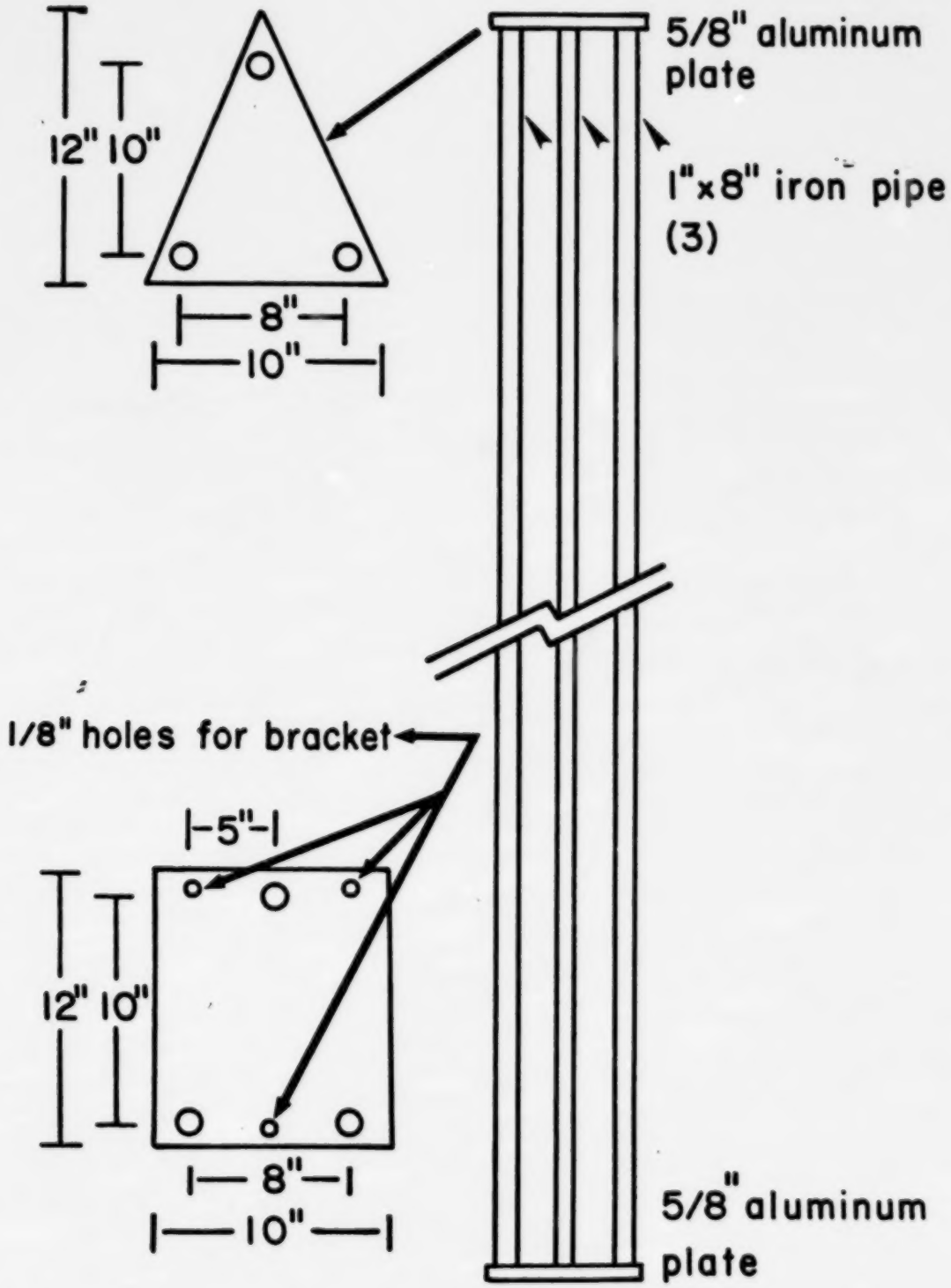


FIGURE 3. DETAILS OF CONCENTRATION PROFILE MAST

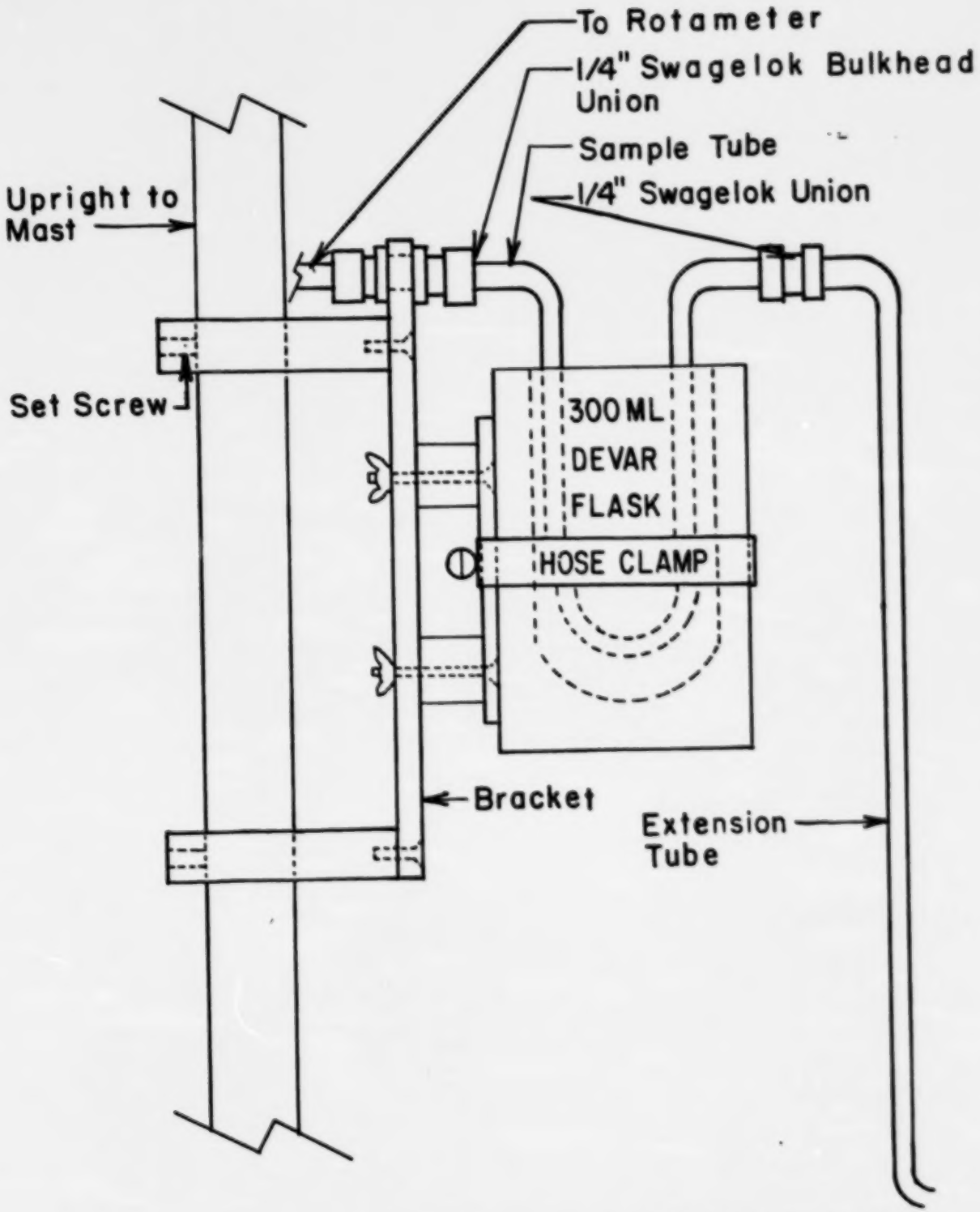


FIGURE 4. DETAILS OF SAMPLING DEVICE

350 ml/min. The common outlet of the rotameters was connected to a 1.25 ft^3 steel vacuum tank.

The vacuum tank was evacuated to 635 mm of mercury. This could be done by means of a built-in hand pump or by attachment to a water powered aspirator. The tank was fitted with a two-way valve and a vacuum gauge. All connections between the pieces of equipment were either 6.35 mm (¼ in.) stainless steel tubing or 11.1 mm (7/16 inch) Tygon tubing. FIGURE 2 shows a schematic representation of the mast in place on a barge with all equipment connected. The mast was secured to a base plate which is then placed on the flat prow of the barge.

Preparatory to the actual sampling, the mast was attached to the base plate and the assembly was placed on the bow of the barge. The six 300 ml Dewar flasks were attached to the mast. The vacuum tank was connected to the rotameter bank. Six sample tubes were connected to the sampling devices, and extensions were added. All connections were tightened with wrenches. The sampling devices were adjusted in height to give sampling heights of between 5 cm. to 2.4 m. The sample heights were spaced in an approximate logarithm pattern with the close spacing being at the bottom. Immediately before sampling, the Dewar flasks were filled with liquid oxygen. The bow of the barge was brought about to face the wind.

To collect a sample, a stopwatch was started and the valve on the vacuum tank was opened. The rotameters were immediately adjusted to read 67, giving a flow rate of 100 ml/min. The flow was allowed to continue for six minutes. At this time, the valve on the vacuum tank was turned off. The tubes were disconnected, their numbers were recorded, and they were capped. Then they were placed in the ice chest containing liquid oxygen.

Wind Measurements

The wind profile system consisted of a 3.3 meter aluminum mast fitted with

six anemometer stations. These stations were spaced at 0.2, 0.4, 0.8, 1.6, 2.4, and 3.2 meters from the bottom of the mast. At the top of the mast was a wind direction sending unit.

The anemometer sending units consisted of three cup anemometers attached to a sensor. The sensor operated photo-electrically to convert revolutions into electrical signals. These signals were fed to a counter via a 100-foot waterproof cable.

The counting units summate impulses from each anemometer separately. A series control adjusts the light intensity in each sensing unit. A separate console records the wind direction continuously on a slow speed strip chart recorder. Power for both the wind speed counting unit and the wind direction recording unit was supplied by a 12-volt lead-acid storage battery. The battery was manufactured by Goodyear and all other equipment was manufactured by Thornthwaite Associates.

In use, the wind speed mast was clamped to the same baseplate as the concentration mast. The counters and chart were moved to a mid-position on the barge for protection. A stopwatch was used to measure the time intervals for wind speed computation.

To measure a wind profile, the amplifier of the counter was turned on for six minutes and then turned off. The new readings were recorded. A continuous record of wind direction was provided by the strip chart recording for the day's samples.

Temperature and Humidity Measurements

The temperature mast was constructed from a television antenna mast. The extended length was 36 feet. Modifications were made to the mast to allow vertical movement of the temperature and humidity probe.

The temperature-humidity probe consisted of a wet and dry bulb thermometer

mounted in a Plexiglas chamber. Inside the chamber was a small, electrical fan to provide flow over the dry and wet thermocouples. A cotton wick wetted by a water reservoir with a metering valve maintained a constant degree of moisture on the wet thermocouple. A six-conductor cable led to the receiving unit.

The receiving unit consisted of an electronic potentiometer calibrated to produce a Fahrenheit temperature on the liquid crystal display. Differences in the wet bulb-dry bulb temperature could be directly read. This provided a means for calculating humidity. The probe and read-out device were manufactured by Atkins Technical, Inc., of Gainesville, Florida.

To measure a temperature profile, the 12 m. (40 ft.) mast was attached to the base plate. The temperature probe was attached to the slide with duct tape. The reservoir for the wet bulb thermometer was filled with distilled water. The receiving unit was turned on to allow the unit to stabilize.

A temperature profile was measured by raising the probe six feet at a time. Dry bulb temperature and wet/dry bulb differences were recorded for each height.

Water Samples

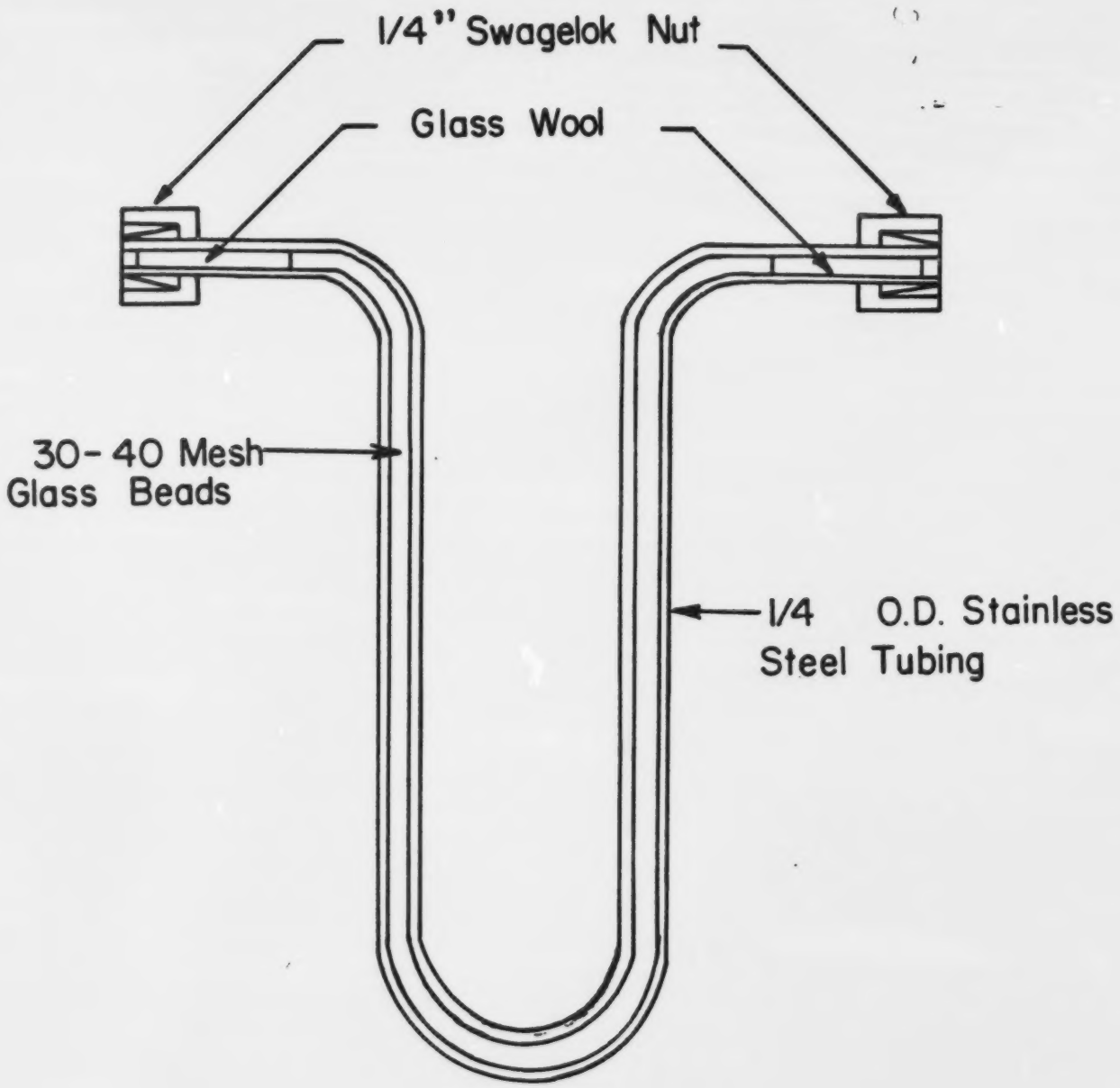
At each air sampling location, a corresponding water sample was collected. A 25 ml sample was taken each time. One drop of concentrated sulfuric acid was added to prevent further bacterial action. The water temperature was measured at the sample location with the use of a glass thermometer.

b. CRYOGENIC SAMPLING AND ANALYSIS

Sampling Tubes

Gas samples were collected cryogenically using 6.35 mm (¼ in.) O.D. stainless steel tubes bent in the shape of a "U", packed with 30-40 mesh glass beads and immersed in liquid oxygen. Details of the tubes are shown in FIGURE 5.

Samples were collected by placing the lower end of the sampling tube in a Dewar flask filled with liquid oxygen and drawing air through the tube at a



Actual Size

FIGURE 5. SECTIONAL VIEW OF SAMPLE TUBE

100 ml/minute for six minutes.

Before being used for sampling, each tube was thermally desorbed and checked by use of a gas chromatograph for cleanliness. After samples were collected, the tubes were capped and stored in liquid oxygen until analysis.

Cryogenic Equipment

Two large, metal evacuated Dewar flasks were used to transport liquid oxygen to sample sites. One of these had a volume of 17 liters, the other had a volume of 10 liters. The smaller Dewar flask was fitted with a low pressure liquid withdrawal device and was used to fill the sample mast Dewar flasks. Both of the large metal Dewar flasks were manufactured by Linde Division of the Union Carbide Company.

A large insulated ice chest was modified for the storage of the collected samples. Two cm. thick styrofoam insulation board was cut to fit flat in the ice chest. Enough pieces were cut to completely fill the chest. Then holes were cut to allow the fitting of three institutional-sized food cans. These were filled with liquid oxygen.

Gas Chromatography

The concentration of acetone, methanol and acetaldehyde was determined using a microprocessor controlled Perkin-Elmer Sigma 3 gas chromatograph fitted with a flame ionization detector (FID). A Perkin-Elmer Minigrator was used to integrate and record the output from the FID. A Houston Instruments recorder was used to plot peaks.

For air samples, a Carle six port, two-way valve of tantulum construction was used to replace the lower injection port. In the first valve position, the carrier gas flows directly through a bypass in the valve, through a capillary trap of 1.6 mm (1/16 in.) stainless steel tubing and into the chromatographic column. In the second position, the carrier gas first sweeps out

the sample tube, then flows through the column. FIGURE 6 shows the details of the valve plumbing.

The column used was a "waterproof" Chromasorb 102 column 2m. (6 ft.) long and 3.2 mm (1/8 in.) in diameter obtained from Supelco.

Carrier gas, helium, was adjusted to give a flow of 50 milliliters per minute. To obtain the correct flow of air, the inlet pressure to the detector was set at 30 PSIG. Likewise, the hydrogen detector inlet pressure was adjusted to 20 PSIG. These parameters were used for both air and water samples.

Temperatures on the gas chromatograph were entered and controlled by a microprocessor. The detector and injector were maintained at 200°C for both air and water samples. The column temperature was set at 140°C for air samples and 150°C for water samples. The temperature was raised 50°C overnight and on weekends to allow the column, detector, and injector to be self-cleaning.

Sample tubes and capillary trap were cooled with liquid oxygen contained in a 300 ml Dewar flask. Sample tubes were thermally desorbed with a 2000 watt, 260°C heat gun and the capillary trap was desorbed with Dow Corning diffusion pump fluid heated to 180°C.

Air samples were run by the following procedure:

1. Sample tubes were attached to the Carle valve via their Swagelok fittings while still in liquid oxygen.
2. Liquid oxygen was transferred to the capillary trap.
3. The Carle valve was turned to the sample position, the heat gun was directed onto the sample tube and the timer on the G.C. was activated simultaneously.
4. Desorption was continued for five hundred seconds to insure complete desorption of the sample.
5. At the end of the desorption period, the Carle valve was turned to

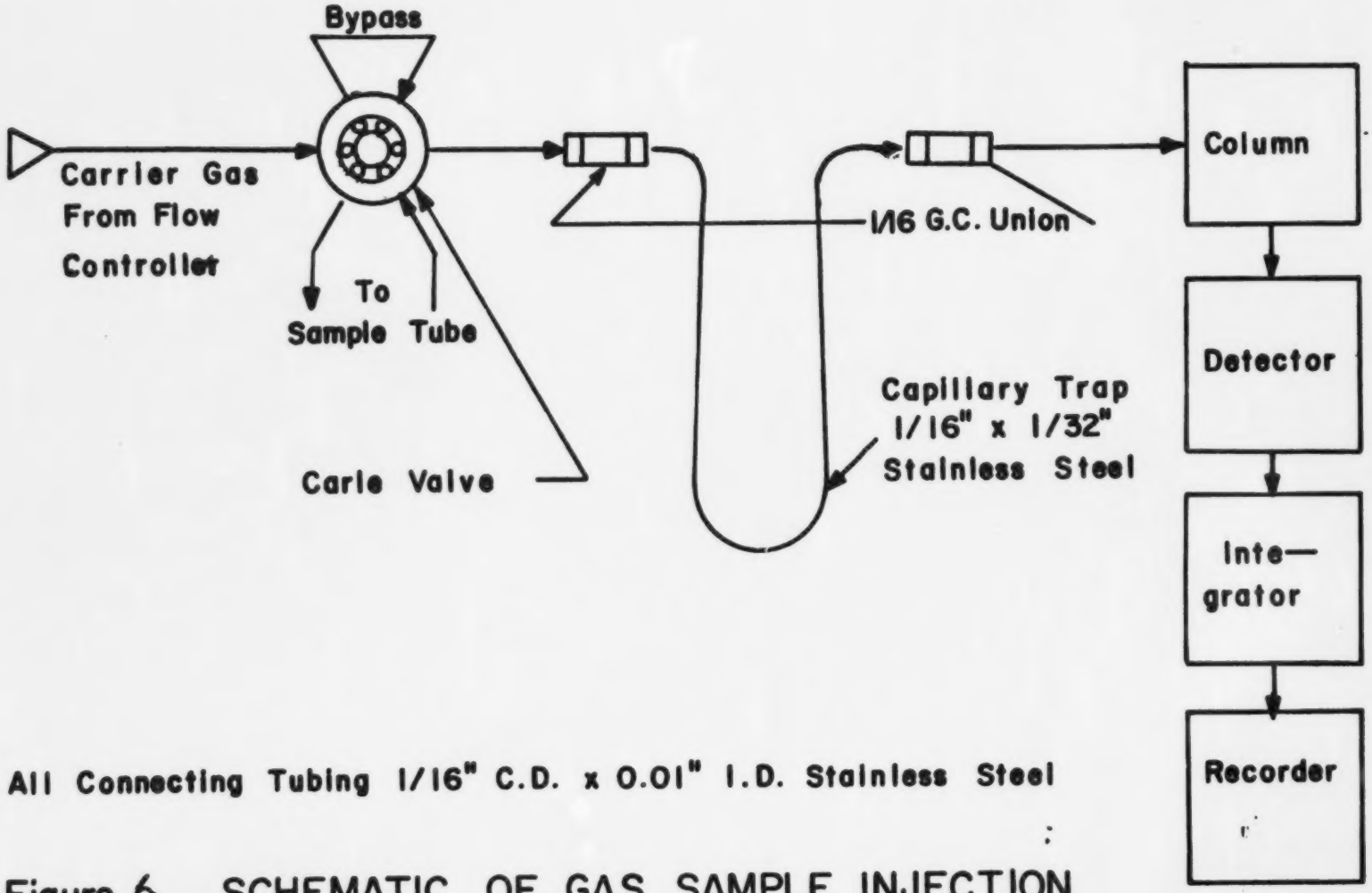


Figure 6. SCHEMATIC OF GAS SAMPLE INJECTION SYSTEM

the bypass position and the heat gun was turned off.

6. The liquid oxygen around the capillary trap was replaced with silicon diffusion fluid heated to 180°C and simultaneously, the auto zero of the G.C. and run button on the integrator were pressed.
7. The chromatograph was recorded for 400 seconds and the retention times of the peaks were used to identify the organic compounds.

Water samples were injected directly into the Chromasorb 102 column. A one microliter aliquot was measured by using a 10 microliter Hamilton syringe.

Calibration of Sampling System

The sampling tube - gas chromatograph system was calibrated by using permeation tubes containing acetone, acetaldehyde, and methanol. The tubes were designed to allow the chemicals to diffuse out into the air at a very slow and relatively constant rate. The emission rate of the tubes were determined gravimetrically.

The permeation tubes were contained in Dynacalibrator ®(model 220-F, from Metronics) control chamber. The Dynacalibrator is essentially a glass chamber surrounded by a thermostatically controlled heater and fitted with a valve and rotameter to control and measure the flow through it. The chamber contained several permeation tubes. Temperature was controlled at 50°C. Flow through the Dynacalibrator was produced by a vacuum pump and controlled with a needle valve. The flows were controlled at 200 milliliters per minute.

To collect a sample from the Dynacalibrator, a sample tube was placed in a Dewar flask of liquid oxygen. Next, one end of the sample tube was connected to the outlet of the Dynacalibrator and the other was connected to the sample suction line. The valve was turned to the sampling position and left there for six minutes to collect a sample. During the entire sampling period, the sample tube remained immersed in liquid oxygen. After the sampling period

was over, the valve was closed and the sample tube was removed from the instrument. The tube was kept in liquid oxygen until it was ready to run.

Chemicals

The pertinent properties of the three pure chemicals measured in this study are presented in TABLE 2.

TABLE 2. CHEMICAL CHARACTERISTICS

Name	Formula	M.W.	Boiling Point, °C	Vapor Pressure mm of Hg at 20°C
Methanol	CH_3OH	32	65	95
Acetone	CH_3COCH_3	58	56	170
Acetaldehyde	CH_3CHO	44	21	760

c. FIELD SAMPLING LOCATIONS

The field test program was performed over the period of February 18, 1980 through June 20, 1980. Four aerated basins adjacent to four pulp and paper mills in central and southeastern Arkansas were sampled. TABLE 3 contains some general information for each basin. All mills were sampled twice.

Mill No. 1 is an integrated, 1270 mt/d, bleached Kraft mill processing pine and hardwood. On March 10, winds were extremely light (i.e., $\leq$ 6.4 km/h and variable from the southwest. Some foam was near the aerators but thinning to a leopard skin appearance. Much of the surface was clear. Wind shifted to southwest and west. The day was sunny and bright, five profiles were obtained. On May 6 the sky was overcast. Dead calm in morning thunderstorms nearby. As day progressed, some light wind (i.e., $\leq$ 13 km/h) developed from the south. Foam on surface to about 30% coverage. The sky

TABLE 3. MILL AERATED STABILIZATION BASIN DATA

	1	2	3	4
Water flow (mgd)	50	30	4	10
Detention time (days)	12.5	13.8	4	25
Depth (feet)	7.5	10	7	10
Surface area (acres)	265	85	7	110
Surface aerators (no.)	25	32	10	8
Power per aerator (hp)	75	75	20	100
Water temperature (^{o}C), Trip 1	25	28	34	36
Water temperature (^{o}C), Trip 2	29	34	36	35
Air temperature (^{o}C), Trip 1	24	20	28	30
Air temperature (^{o}C), Trip 2	27	25	24	27
Wind speed (mi/h), Trip 1	2.8	16	7.4	11
Wind speed (mi/h), Trip 2	4.4-8.0*	13	7.5	6.2-12*
Methanol in water (mg/l) -1	26	17	12	10
Methanol in water (mg/l) -2	15	29	-	6.9

* Denotes morning and afternoon values.

cleared at noon and six profiles were obtained.

Mill No. 2 is also a bleached Kraft mill with a production of 1820 mt/d. On April 7 there was a steady, fairly high wind from the southeast. Foam covered about 50% of the water surface. Two profiles were obtained from 2:55PM to 4:30PM. On April 8, three more profiles were obtained from 1:30PM to 3:10PM. The wind was strong in morning. Airport weather reported eighteen knots with gusts to 20 knots, causing much blowing foam and white caps. By noon, the winds had subsided somewhat so that sampling was possible. Surface was

partially covered with foam, particularly downwind of the aerators. See TABLE 6 for specific conditions.

Trip No. 2 to Mill No. 2 was on May 29. Winds were brisk from the southwest and the sky was overcast (85% coverage). There was very thick (20 cm.) foam on the water inlet end of the basin, decreasing to light foam near the outlet. The skies were clear at noon. Four profiles taken in morning and two in the afternoon.

Mill No. 3 is a 320 mt/d, unbleached pulp and paper Kraft mill. On May 30, three profiles were obtained. Wind was light from the south with overcast skies. Winds were variable with foam on 15% of the lagoon surface. Trees of 9 to 12 m. in height were on the south side of the lagoon. Aerodynamic height to fetch ratio was not satisfied since sampling was done about 15 to 30 m. from the tree-line. Trip No. 2 was on June 20. Skies were overcast with some drizzle and light winds. The wind was from the northeast. There was a foam layer of 8 centimeters on 75% of the surface. No temperature profiles obtained at this mill due to small size of the available water craft. Most aerators were off during the sampling for safety purposes.

Mill No. 4 is a 420 mt/d facility for Kraft pulping. On May 28, the weather was partly cloudy and winds variable from the southeast and south. The basin had 60% to 70% foam coverage. Four profiles were obtained. Trip No. 2 was on June 19. Skies were overcast and the wind was from the west. In the afternoon, partly cloudy conditions prevailed and the wind from the south, southwest.

SECTION 5

RESULTS AND DISCUSSION

a. CONCENTRATIONS IN THE AIR

It is of interest to establish the range of chemical concentrations observed in the aerodynamic boundary layers above the respective wastewater treatment basins. TABLE 4 summarizes the concentrations of methanol, acetone and total hydrocarbon (GC/FID) at each site and for each trip. With few exceptions, the maximum concentration was observed at the lowest sample point which was usually a few centimeters above the water surface. The maximum reported concentration is that single high value observed for that chemical on that particular trip. The average value reported represents all samples at all heights. Average values of the concentration at the uppermost sample point, usually two meters above the water surface, are also given in the table. It is apparent from this table of concentrations that the water surface is the source of the volatile chemicals. FIGURE 7 is an illustration of a typical profile. This variation with height reflects the general characteristics of the thirty-eight profiles obtained in the field. Based on peak area, at least sixty to eighty-five percent of the total hydrocarbon fraction was methanol.

b. EMISSION RATES FROM BASINS AND STATISTICAL ANALYSIS OF FIELD DATA

Flux measurements based on Equation 24 are summarized for each mill in TABLE 5 for methanol, acetone and total hydrocarbon. TABLES 6 through 9 contain wind and chemical profile results, statistical parameters, Richardson numbers and individual profile flux results.

Graphs of each profile, similar to those shown in FIGURE 7, were prepared for each chemical. Data points reflecting obvious erroneous chemical analysis

TABLE 4. CONCENTRATIONS IN THE BOUNDARY LAYER

Site/Trip	Parameter	Methanol (ng/l)	Acetone (ng/l)	Total Hydrocarbon (ng/l)
Mill 1, Trip 2	maximum	868	51.9	1020
	average	271	23.9	655
	at 2 meters	101	11.6	199
Mill 1, Trip 3	maximum	3400	81.6	3540
	average	1130	44.1	1360
	at 2 meters	522	22.6	543
Mill 2, Trip 1	maximum	1180	22.9	1260
	average	612	18.2	773
	at 2 meters	636	10.3	443
Mill 2, Trip 2	maximum	2090	52.6	3150
	average	768	35.3	902
	at 2 meters	48.5	8.5	66.9
Mill 3, Trip 1	maximum	366	26.0	569
	average	233	19.5	-
	at 2 meters	51.8	7.4	-
Mill 3, Trip 2	maximum	359	153	1280
	average	85.3	35.0	336
	at 2 meters	22.5	13.1	66
Mill 4, Trip 1	maximum	2030	43.6	2120
	average	807	33.1	1130
	at 2 meters	23.8	-	127
Mill 4, Trip 2	maximum	481	43.3	1260
	average	231	31.8	484
	at 2 meters	55.7	6.7	363

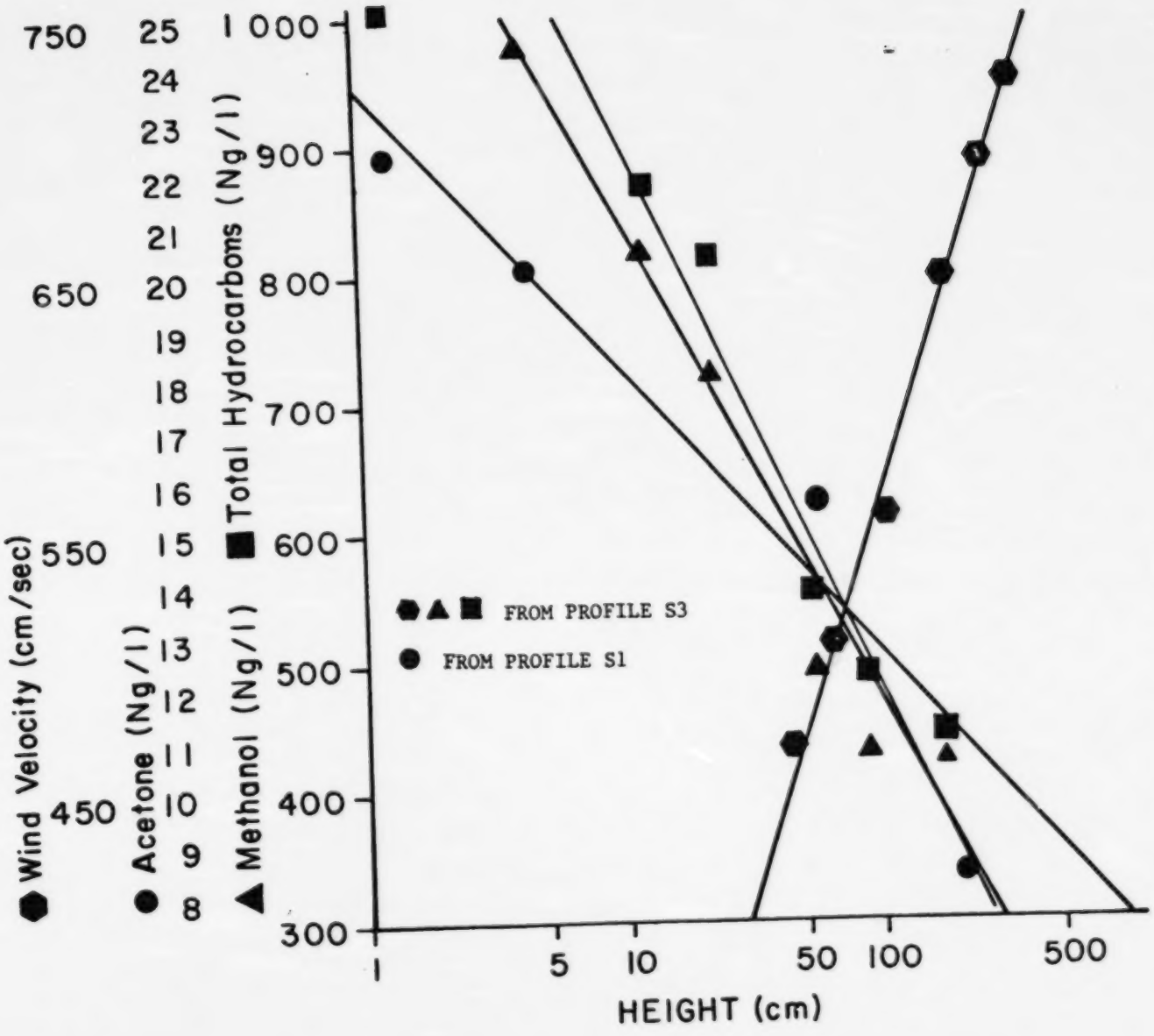


Figure 7. Field data from mill 2 sample trip 1.

TABLE 5. ORGANIC CHEMICAL EMISSIONS

Parameter	Mill 1	2	3	4
Detention time (days)	12.5	13.8	4	24
Surface area (acres)	265	85	7	110
Surface aerators (number)	25	32	10	8
Methanol emission(tons/day)	2.7	1.2	.011	0.61
Methanol flux (lbs/day·acre)*	20	29	3.2	11
Acetone emission(lbs/day)	200	39	2.5	24
Acetone flux (lbs/day·acre)*	.77	.46	.36	.22
Total hydrocarbon† (tons/day)	4.4	1.1	.042	1.3
Total hydrocarbon† (lbs/day·acre)*	33	25	12	23

† GC/FID

* Flux rate $ng/cm^2 \cdot s$ = (lbs/day·acre) ÷ 7.70.

TABLE 6. SAMPLE PROFILE SLOPE AND STATISTICAL REGRESSION PARAMETERS

MILL NO. 1

Sample Number	Number of Observations n	Variable, Velocity or Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
2-S1	5	Wind	13.4	3.60	.974	7.45	-.507
	3	Methanol	-99.43	.987	.987		-.507
	4	Acetone	-1.93	.596	.983	-7.68	-.507
	4	Total Hyd.	-114.	30.3	.988	-8.91	-.507
2-S2	4	Wind	1.0	.275	.981	7.14	-24.8(?)
	5	Methanol	119.	117.	.773	2.11	-24.8(?)
	5	Acetone	-6.14	4.73	.919	-4.05	-24.8(?)
	6	Total Hyd.	-186.	143.	.898	-4.08	-24.8(?)
2-S3	5	Wind	25.4	4.0	.99	12.5	0.0
	4	Methanol	-301.	43.8	.987	-8.63	0.0
	3	Acetone	-7.38		.929		0.0
	4	Total Hyd.	-222.	63.4	.983	-7.58	0.0
2-S4	3	Wind	72.75		.992		-.357
	5	Methanol	-191.	147.	.929	-4.33	-.357
	4	Acetone	-11.9	11.9	.858	-2.36	-.357
	3	Total Hyd.	-147.3		.936		-.357
2-S5*	4	Wind	6.39	1.63	.983	7.63	-1.88
	3	Methanol	-37.8		.983		-1.88
	4	Acetone	-.984	2.89	.529	-.882	-1.88
	4	Total Hyd.	-68.1	17.8	.990	-9.88	-1.88
3-S1	6	Wind	22.4	.617	.999	62.1	+.311
	5	Methanol	-218.	329.	.820	-2.48	+.311
	6	Acetone	-13.7	10.1	.931	-5.10	+.311
	4	Total Hyd.	-437.	280.	.936	-3.77	+.311

†S_v is cm/s and S_ρ in ng/l.
*Denotes significant up-wind surface discontinuity at sample site.

TABLE 6 (cont.)

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
3-S2		Wind	53.3				-.106
	6	Methanol	-468.	554	.718	-2.06	-.106
	6	Acetone	-7.23	14.4	.523	-1.23	-.106
	5	Total Hyd.	-934.	729.	.816	-2.45	-.106
3-S3*	6	Wind	67.0	6.35	.994	18.1	-.137
	3	Methanol	-955.		.979		-.137
	3	Acetone	-21.0		.100		-.137
	4	Total Hyd.	-416.	239.	.869	-2.48	-.137
3-S4	6	Wind	38.9	4.50	.991	14.8	-.0871
	6	Methanol	-754.	421.	.945	-5.76	-.0871
	6	Acetone	-15.5	673.	.037	.0737	-.0871
	6	Total Hyd.	-753.	338.	.963	-7.16	-.0871
3-S5	6	Wind	57.9	1.24	1.000	80.1	-.0343
	4	Methanol	-92.6	130	.817	-2.00	-.0343
	4	Acetone	-9.88	9.75	.896	-2.86	-.0343
	4	Total Hyd.	-137.	154.	.871	-2.50	-.0343
3-S6*		Wind	60.2	9.53	.983	10.8	-.0333
	5	Methanol	-52.1	25.2	.940	-4.78	-.0333
	6	Acetone	1.11	9.09	.134	.270	-.0333
	5	Total Hyd.	-47.0	36.8	.863	-2.95	-.0333

†S_v in cm/s and S_ρ in ng/l. *Denotes significant up-wind surface discontinuity at sample site.

TABLE 7. SAMPLE PROFILE SLOPE AND STATISTICAL REGRESSION PARAMETERS

MILL NO. 2

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_p	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
1-S1*	3	Wind	63.48		.963		-.00933
	5	Methanol	-197.	129.0	.962	-6.14	-.00933
	4	Acetone	-2.54	2.08	.961	-4.91	-.00933
	5	Total Hyd.	-186.	158.	.939	-4.73	-.00933
1-S2	6	Wind	209.	135.	.812	2.79	-.0148
	4	Methanol	-166.	70.6	.976	-6.29	-.0148
	3	Acetone	-.70		.437		-.0148
	3	Total Hyd.	-170.4		.968		-.0148
1-S3	6	Wind	130.	7.97	.998	29.3	-.014
	6	Methanol	-167.	50.6	.980	-9.97	-.014
	5	Acetone	-.227	1.54	.199	-.351	-.014
	6	Total Hyd.	-185.	45.6	.987	-12.2	-.014
1-S4	6	Wind	134.	7.43	.998	32.2	-.0169
	5	Methanol	-252.	18.8	.998	-31.52	-.0169
	5	Acetone	-3.47	1.73	.938	-4.71	-.0169
	5	Total Hyd.	-234.	69.9	.977	-7.90	-.0169
1-S5*	3	Wind	110.		.989		-.00577
	4	Methanol	-159.	22.3	.978	-6.69	-.00577
		Acetone					-.00577
	4	Total Hyd.	-191.	31.9	.970	-5.62	-.00577
2-S1	6	Wind	68.8	4.12	.998	29.3	-.00465
	5	Methanol	-135.	353.	.520	-1.05	-.00465
		Acetone					-.00465
	5	Total Hyd.	-174.	459.	.517	-1.05	-.00465

TABLE 7 (cont.)

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
2-S2	6	Wind	67.8	4.83	.997	24.6	-.013
	5	Methanol	-16.2	147.	.154	-.270	-.013
	4	Acetone	1.29	3.60	.465	.742	-.013
	3	Total Hyd.	14.1		.270		-.013
2-S3	6	Wind	81.2	5.80	.997	24.6	-.00197
	5	Methanol	-220.	335.	.730	-1.85	-.00197
	4	Acetone	-3.36	2.48	.927	-3.49	-.00197
	4	Total Hyd.	-231.	388.	.734	-1.53	-.00197
2-S4*	6	Wind	72.6	3.71	.998	34.3	-.00749
	5	Methanol	-281.	118.	.950	-5.24	-.00749
	4	Acetone	-7.72	2.17	.984	-7.73	-.00749
	5	Total Hyd.	-298.	101.	.966	-6.49	-.00749
2-S5	6	Wind	109.	5.88	.998	32.4	-
	5	Methanol	-163.	941.	.298	-.541	-
	3	Acetone	-7.50		.340		-
	6	Total Hyd.	-440.	984.	.598	-1.49	-
2-S6	6	Wind	97.6	6.24	.997	27.4	-.0267
	6	Methanol	-236.	569.	.534	-1.26	-.0267
	4	Acetone	-8.53	2.96	.979	-6.72	-.0267
	5	Total Hyd.	-142.	625.	.327	-.600	-.0267

† S_v is cm/s and S_ρ in ng/l. *Denotes significant up-wind surface discontinuity at sample site.

TABLE 8. SAMPLE PROFILE SLOPE AND STATISTICAL REGRESSION PARAMETERS

MILL NO. 3

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
1-S1*	4	Wind	72.1	6.87	.989	9.45	-‡
	5	Methanol	-75.1	80.9	.834	-2.62	-
		Acetone					-
	4	Total Hyd.	-87.6	226.	.580	-1.01	-
1-S2*	6	Wind	50.3	2.28	.998	34.9	-
	5	Methanol	-109.	82.4	.853	-2.83	-
	4	Acetone	-11.4	6.72	.899	-2.90	-
	5	Total Hyd.	341.	911.	.420	.802	-
1-S3*	6	Wind	64.4	3.98	.997	25.6	-
	5	Methanol	-5.62	185.	.043	-.0754	-
	3	Acetone	-2.44		.802		-
	5	Total Hyd.	98.7	183.	.646	1.47	-
2-S1	5	Wind	80.3	1.48	1.00	92.2	-
	6	Methanol	-8.93	21.0	.619	-1.58	-
	5	Acetone	-2.02	2.12	.897	-3.51	-
	5	Total Hyd.	-57.7	35.7	.887	-3.32	-
2-S2	5	Wind	99.5	6.48	.997	24.7	-
	6	Methanol	-10.3	22.3	.578	-1.42	-
	5	Acetone	-3.98	2.30	.896	-3.49	-
	6	Total Hyd.	-57.3	55.6	.845	-3.16	-
2-S3	5	Wind	143.	5.39	.999	44.9	-
	5	Methanol	-78.4	94.7	.809	-2.39	-
	5	Acetone	-1.84	4.13	.539	-1.11	-
	5	Total Hyd.	-379.	179.	.956	-5.67	-

TABLE 8 (cont.)

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
2-S4	5	Wind	56.1	7.39	.991	12.9	-
	5	Methanol	-10.7	12.3	.835	-2.63	-
	5	Acetone	-.727	2.09	.465	-.910	-
	6	Total Hyd.	-17.2	89.2	.282	-.588	-
2-S5*	5	Wind	54.2	3.43	.998	26.8	-
	6	Methanol	-31.4	16.3	.959	-6.73	-
	5	Acetone	-241.	182.	.863	-2.96	-
		Total Hyd.					

†S_v in cm/s and S_ρ in ng/l. *Denotes significant up-wind surface discontinuity at sample site.
‡No temperature profiles taken.

TABLE 9. SAMPLE PROFILE SLOPE AND STATISTICAL REGRESSION PARAMETERS

MILL NO. 4

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope † S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
1-S1	6	Wind	97.7	3.62	.999	42.7	+.0107
	6	Methanol	-156.	265.	.733	-2.15	+.0107
	5	Acetone	-.669	6.87	.182	-.321	+.0107
	6	Total Hyd.	-166.	302.	.709	-2.01	+.0107
1-S2	6	Wind	61.4	3.56	.997	27.3	-.0823
	6	Methanol	.266E29	.301E29	.994	17.8	-.0823
	4	Acetone	.133	8.31	.022	.0306	-.0823
	5	Total Hyd.	-593.	160.	.979	-8.31	-.0823
1-S3	6	Wind	77.6	3.64	.998	33.7	-.00811
	5	Methanol	-416.	124.	.945	-5.01	-.00811
	3	Acetone	2.80		.150		-.00811
	4	Total Hyd.	-570.	205	.946	-4.14	-.00811
1-S4*	6	Wind	55.1	2.48	.998	35.1	-.00519
	4	Methanol	-84.6	154	.575	-.993	-.00519
	2	Acetone	-2.11		1.0		-.00519
	4	Total Hyd.	-675.	23.8	.973	-5.96	-.00519
2-S1*	6	Wind	44.2	2.61	.997	26.8	+.0554
	5	Methanol	-16.4	25.0	.708	-1.74	+.0554
	5	Acetone	-3.50	2.55	.909	-3.78	+.0554
	6	Total Hyd.	-22.6	46.2	.568	-1.38	+.0554

TABLE 9 (cont.)

Sample Number	Number of Observations n	Variable, Velocity of Concentration	Slope† S_v or S_ρ	Standard Error of the Estimate s_E	Multiple Correlation Coefficient r	T-Value for Slope t	Richardson Number R_i
2-S2	3	Wind	83.31		.907		+.00808
	5	Methanol	-67.7	46.3	.931	-4.42	+.00808
	3	Acetone	-4.80		.971		+.00808
		Total Hyd.	-57.7		.232		+.00808
2-S3	6	Wind	88.4	5.69	.997	24.6	+.00657
	6	Methanol	-88.5	129.	.743	-2.22	+.00657
	6	Acetone	-2.83	10.5	.400	-.874	+.00657
	5	Total Hyd.	-100.	121.	.838	-2.66	+.00657
2-S4	6	Wind	72.3	4.14	.997	27.6	+.143
	6	Methanol	-31.4	26.1	.890	-3.89	+.143
	5	Acetone	-8.68	6.30	.932	-4.49	+.143
	6	Total Hyd.	-41.6	34.4	.891	-3.92	+.143

† S_v in cm/s and S_ρ in ng/l. *Denotes significant up-wind surface discontinuity at sample site.

were discarded. Erroneous analyses were often due to improper GC integrator-peak separation, leaks in the sample line downstream of the U-tube traps and inadvertent dipping of the extension tube into the water or the foam layer.

Each set of from 4 to 6 observations was processed on a statistical linear regression computer program. The slope (with appropriate sign), standard error of the estimate, multiple correlation coefficient (one dependent variable only) and the t-value for the slope (with appropriate sign) were extracted from the print-out and appear in TABLES 6 through 9. A few sets with two or three good observations per set were processed by hand and no statistics were reported.

The slopes reported in column 4 of TABLES 6 through 9 were based on all the selected data within the two-meter boundary layer. In almost all instances, the wind profiles (i.e., $\bar{v}_x$ vs. ln y) were perfectly linear and this was the basis on which the decision to use all the data was made. Data scatter inherent in the chemical profiles precluded any detection of non-linearity from the respective graphs. As can be seen in column 6 of TABLES 6 through 9, the correlation coefficient for the wind profiles are very near unity in most cases and always greater than that for the chemical profiles. On occasion, chemical profile slopes were positive (see methanol in sample 2-S2). This suggests that methanol is being absorbed by the water surface at this point on the basin.

The Richardson number calculation appears in column 8 of TABLES 6 through 9. This number was calculated from two dry bulb temperatures and two wind velocity observations at approximate heights of 20 cm and 200 cm above the water surface using Equation 18. All conditions of stability were encountered. No temperature profiles were taken at the Mill 3 site. The available boat at this site was too small to accomodate the temperature profile apparatus. Neutral stability was assumed in making the flux calculation for Mill 3.

Individual flux calculations for each profile appear in TABLE 10. The

TABLE 10. MEASURED CHEMICAL FLUX RATES FROM WATER SURFACE

Mill and Sample No.	Stability Correction $\{\phi_m^2 S_{c_{Al}}^{(t)}\}^{-1}$	Flux Rate, ($ng/cm^2 \cdot s$) Methanol	Acetone	Hydrocarbon	Comments
1-2-S1	5.13	.78	.013	.89	
S2	1.0	-.014†	.00061	.021	Ri beyond range
S3	1.00	.87	.019	.64	
S4	4.34	6.9	.38	5.3	
S5*	9.74	.27	.0061	.48	
1-3-S1	.246	.14	.0076	.27	
S2	2.51	7.1	.097	14.	Acetone chemistry?
S3*	2.80	20.	.39	8.9	Acetone chemistry?
S4	2.31	7.7	.14	7.7	Acetone chemistry?
S5	1.65	1.0	.095	1.5	
S6*	1.63	.58	-.011	.52	Acetone chemistry?
2-1-S1*	1.21	1.7	.021	1.6	
S2	1.32	5.2	.019	5.3	
S3	1.30	3.2	.0039	3.5	Acetone chemistry?
S4	1.36	5.2	.063	4.9	
S5*	1.14	2.3	-	2.7	
2-2-S1	1.11	1.2	-	1.5	Methanol chemistry?
S2	1.29	.16	-.011	-.14	All chemistry?
S3	1.05	2.1	.029	2.2	
S4*	1.17	2.7†	.066	2.9†	
S5	-	2.0†	.082†	5.5†	All chemistry?
S6	1.53	4.0	.13	2.4†	Methanol chemistry?
3-1-S1*	-	.62†		.72†	Total hydrocarbon chemistry?
S2*	-	.62†	.057†	1.95†	Total hydrocarbon chemistry?
S3*	-	.041†	.016†	-.72†	Methanol chemistry?
3-2-1	-	.082†	.016†	.53†	
S2	-	.12†	.040†	.65†	Methanol chemistry?
S3	-	1.3†	.026†	6.2†	Acetone chemistry?
S4	-	.068†	.0041†	.11†	Acetone & hyd. chemistry?
S5*	-	-	.17†	1.5†	
4-1-S1	.807	1.4	.0053	1.5	Acetone chemistry?
S2	2.26	-	-.0018	9.4	Acetone chemistry?
S3	1.18	4.3	-.026	5.9	Acetone chemistry?
S4*	1.12	.59	.013	4.7	Methanol chemistry?
4-2-S1*	.515	.042	.0080	.059	Total hydrocarbon chemistry?
S2	.844	.54	.034	.46	
S3	.868	.77	.022	.87	Acetone chemistry?
S4	.350	.090	.022	.12	

† Denotes flux rate with stability correction factor of unity.

* Denotes significant upwind surface discontinuity at sample site.

stability correction factor in column 2 was obtained from Equation 25. Diffusivity corrections are as follows: $(\mathcal{D}_{B1}/\mathcal{D}_{A1})^{2/3}$ = 0.711 for methanol, 0.626 for acetone and 0.711 for total hydrocarbon.

No major surface discontinuities were present on or near the lagoon surfaces upwind of the sample sites except on May 30 at Mill No. 3. Most profiles were obtained at locations where height-to-fetch ratios were at least 1 to 50. Profiles near the berm where this ratio was not present are noted by superscript in column 1 of TABLE 10.

The individual flux measurements in TABLE 10 were reviewed and only those values meeting certain statistical, Ri and height-to-fetch ratio criteria were used to obtain the selected observations summary results in TABLE 11. Column 6 of TABLE 10 contains the appropriate comment by which data was excluded. Chemistry data with correlation coefficients of less than 0.8 were excluded. TABLE 11 also contains a summary of all observations of the flux. The values for Mill No. 3 are only approximate because neutral stability was assumed. It appears that the methanol flux is roughly 2 ng/cm^2·s (16 lbs/acre·day), acetone is .06 ng/cm^2·s (0.46 lbs/acre·d) and total hydrocarbon is 3 ng/cm^2·s (23 lbs/acre·day).

The range of the respective fluxes reported in the selected observations column of TABLE 11 should not be interpreted as a confidence interval. The reported values in this table for a particular chemical in a particular basin reflect fluxes measured under drastically different environmental conditions. Point values of the flux are strong functions of chemical concentration in the water, water temperature and wind speed. Concentration and water temperature change significantly from basin inlet to basin outlet. Wind, as will be discussed in the next section, regulates transport significantly.

Repeated observations at a single point on one basin were not made; however,

TABLE 11. VOLATILE CHEMICAL EMISSION FLUX SUMMARY

Mill Number and Chemical	Selected Observations n	Selected Observations Flux ($ng/cm^2 \cdot s$)	Selected Observations Flux Range	All Observations n	All Observations Flux ($ng/cm^2 \cdot s$)	All Observations Standard Error of Flux
1-methanol	7	2.6	.14-7.7	11	4.1	6.1
1-acetone	5	.10	.0076-.38	11	.11	.15
1-total hydrocarbon	7	4.3	.27-14.	11	3.2	4.7
2-methanol	4	3.8	2.1-5.2	11	2.7	1.6
2-acetone	4	.060	.019-.13	9	.045	.044
2-total hydrocarbon	6	3.2	1.5-5.3	11	2.9	1.7
3-methanol	-	-	-	7	.41	.47
3-acetone	-	-	-	7	.047	.057
3-total hydrocarbon	-	-	-	8	1.5	2.0
4-methanol	5	1.4	.09-4.3	7	1.1	1.5
4-acetone	2	.028	.022-.034	8	.0096	.018
4-total hydrocarbon	6	3.0	.12-9.4	8	2.9	3.4

some insight into the degree of reproducability of the method can be obtained from studying the results for methanol for the first visit to Mill No. 2 (sample No. 2-1 in TABLE 10). High winds in the morning (white caps were present) likely mixed the water in the basin so that the entire surface was at a uniform methanol concentration and temperature. Brisk, steady winds were present when the five profiles were obtained at various locations on the basin. Apparently GC chemical separation and air leaks were minimal for this sortie also. Considering all observations, the average flux was 3.4 $ng/cm^2 \cdot s$ with a standard deviation of 1.7 $ng/cm^2 \cdot s$. Conditions were not as ideal on the second trip to this site, where the average flux was 2.0 $ng/cm^2 \cdot s$ with standard deviation of 1.3 $ng/cm^2 \cdot s$. When all doubtful data is disregarded, the average flux at the site combining both visits is 3.8 $ng/cm^2 \cdot s$, with a range of 2.1-5.2 $ng/cm^2 \cdot s$.

c. ADVANTAGES AND LIMITATIONS OF THE CONCENTRATION PROFILE TECHNIQUE

Advantages

1. The method has a well developed theory. The model originates from Prandtl's mixing length theory of turbulent transport in fluid mechanics. Appropriate empirical constants and correction factors based upon micrometeorological observations yield the final form of the working equations. Section 3b presents the critical details of the theory.
2. The method has a history of applications. The log profile structure, a consequence of the mixing length theory, has been verified in numerous fluid dynamic situations. The method has been used to measure the flux rate of water vapor, carbon dioxide, and pesticides above soil surfaces by agricultural scientists.
3. The method does not disturb the environment being sampled. By sampling

the air boundary layer immediately down-wind of the area source, the procedure does not interfere with the natural transport process on either side of the air-water interface. In contrast, the "box-on-the-water" method disrupts the natural desorption process at the interface due to the presence of the box.

4. The method is amenable to different sampling methods such as cryogenic, solid adsorbent or liquid absorbent traps and trains. The technique could be adapted to measure particulates by using iso-kinetic sampling.

5. The method uses simple equipment and procedures. The velocity and temperature profile instrumentation is off-the-shelf technology. The chemical profile involves trapping, concentration and laboratory analysis. On-going development will simplify and enhance the reliability of the chemical profile procedure.

6. The method is self-checking. When properly operated and six or more observations are made in the two meter air boundary layer, the data, including velocity, temperature and concentrations, should display a linear or near linear behavior when graphed as a function of log of sample height. See Equations 21 and 23.

7. The method should be independent of background or up-wind concentrations or sources. This is a characteristic of gradient methods. The flux is related to the levels of the differences in concentrations rather than the absolute values of concentrations.

8. The method is capable of detecting chemical movement into as well as out of wastewater basins or surface sources. The sign of the slope of the ρ_{A1} vs. ln y graph will relate the direction of the flux of the chemical. A negative slope results if the chemical is being

emitted from the surface and a positive slope results if the chemical is being sorbed onto or into the surface.

Disadvantages

1. The method should be used in the air boundary layer very near the source, in the case of emissions, such that $|Ri| < 4.0$. In general, sampling should be done in the region ($5\ cm < y < 2m$) above the air-water interface.
2. Sampling must be done well down-wind of profile disturbing structures such as high levees, trees, or buildings. Such structures distort the profiles from the shape needed to properly apply the model. h/f (i.e., height-to-fetch ratio) of 50 to 100 should be maintained.
3. The method is applicable to fairly large area emission sources. Only if the h/f ratio can be maintained for the edge, berm, tank rim, etc., should the method be applied to clarifiers, aeration tanks, API separators and other such small area sources.
4. The method is based on average observations of velocity, temperature and concentration and not on instantaneous values. Sample time for $\bar{v}_x$, $\bar{T}$, and $\bar{\rho}_{A1}$ should be 10 to 15 minutes or longer. Longer times, up to 30 minutes, may be appropriate for low windspeed and warm water surfaces. For brisk wind, the shorter times seem to be sufficient.

SECTION 6

A PREDICTIVE MODEL FOR DESORPTION

a. INTRODUCTION AND THE NEED FOR PREDICTIVE MODELS

Desorption models with the capability of making predictions of the emission rate of selected chemicals from wastewater basins have been available since 1974. These models employ mass transport theory concepts. Inputs consist of concentration of the chemical in the water, water temperature, Henry's law constant, wind speed, air temperature, depth of the water, surface area of the basin, number and size of surface aerators, etc.

Although these models have been proposed none have been verified for use with large surface impoundments such as aerated stabilization basins. The need for field-verified desorption models is apparent. The relative cost of a reliable prediction will likely be orders of magnitude less than a field measurement whether by the concentration profile method or other techniques.

The following items will be presented in this section:

- Background, structure, and detailed working equations of a predictive model will be presented. The model consists of ten equations and one table. Although the flux rate is obtained from a simple expression (Eq. 26) much effort need be expended in calculating the correct transport coefficient, K_1. Sufficient details are given so that this document can be used as a basis for building a model.

- Model predictions of the desorption rates of methanol from the four wastewater treatment basins of this study are made.

- A discussion of the predicted vs. measured rates for methanol is presented along with the needs for more field verification work.

b. MODEL DEVELOPMENT

Steady-state desorption of volatile chemicals from aerated stabilization basins was developed by Thibodeaux and Parker (1974). Flux equations, the two resistance theory and individual mass-transfer coefficient relationships were presented for the case of pure desorption. To develop the model, it was necessary to divide the surface into a turbulent zone and a natural zone. The turbulent zone was that area of the basin dominated by the mixing action of mechanical surface aerators while the natural zone was the area influenced by natural processes such as surface winds.

A study of eleven model chemicals and thirteen basins suggested that without biochemical reaction significant volatilization could occur. Predictions were that 58% acetaldehyde, 34% acetone and 10% methanol placed in the basin was stripped. The basic model for pure desorption was modified for biochemical reaction by Thibodeaux (1975). By employing simple first-order biochemical oxidation rate equations, the influence of bioreaction was included and shown to reduce emissions significantly; acetaldehyde stripping was reduced to 35%, acetone to 20%, and methanol to 5%. The role of high concentration of biosolids emerged as an important variable for control of volatile emissions. Freeman (1979, 1980) updated the basic desorption model and incorporated more realistic bio-oxidation rate equations. He found that not more than 0.3% of acrilonitrile was stripped in an activated sludge reactor if the oxygen content is maintained at 2 ppm or greater.

The current version of the desorption model will be developed for the conditions under which the pulp and paper industry surface impoundments were operated. Although the development will involve methanol, the model applies for all volatile or semi-volatile substances. If the basin desorption process is assumed to be at steady-state, the flux rate of methanol ($ng/cm^2 \cdot s$) from

a water surface of mole fraction concentration x is

$$n = MK_l(x-x^*) \tag{26}$$

where: M is the molecular weight of methanol

K_l is overall liquid phase mass-transfer coefficient for methanol in $mol/cm^2 \cdot s$

x^* is the methanol mole fraction in equilibrium with a mole fraction concentration of methanol in air, y. If there is assumed to be no methanol in the air above the basin, then $x^* \equiv 0$.

For a basin with the surface divided into two zones, turbulent and natural

$$K_l = ({K_l}^t A_t + {K_l}^n A_n)/(A_t + A_n) \tag{27}$$

where: ${K_l}^t$ and ${K_l}^n$ are the overall mass-transfer coefficients for the turbulent and natural zones, respectively

A_t and A_n are the turbulent and natural surface areas in cm^2.

The overall coefficients are obtained from the individual phase mass-transfer coefficients through the two resistance theory:

$$\frac{1}{{K_l}^t} = \frac{1}{{k_l}^t} + \frac{1}{H{k_g}^t} \tag{28}$$

and

$$\frac{1}{{K_l}^n} = \frac{1}{{k_l}^n} + \frac{1}{H{k_g}^n} \tag{29}$$

where: k_l^t and k_l^n are the individual liquid phase coefficients

k_g^t and k_g^n are the individual gas phase coefficients

H is Henry's Law constant in mole fraction form:

$$y = Hx \tag{30}$$

TABLE 12 contains Henry's Law constants for methanol in water.

TABLE 12. HENRY'S LAW CONSTANTS FOR METHANOL IN WATER

Temperature, °C	H*
15	0.105
20	0.16
25	0.24
30	0.305
35	0.41
40	0.54
45	0.71
50	0.90

* Henry's Law: y = Hx from Blackwell (1978)

The individual coefficients can be obtained from the following empirical relationships. $k_1{}^t$ can be predicted using agitator manufacturers' oxygenation rate data correlated by the following equation (Thibodeaux, and Parker, 1974):

$$k_1{}^t a_v = 6.06E3 \sqrt{\frac{D_{A_1W}}{D_{O_2W}}} N_{O_2} E\omega\alpha\, 1.024^{T-20^oC}/V \qquad (31)$$

where: $k_1{}^t a_v$ is lb mol/hr·ft^3

D_{A_1W} is the molecular diffusivity of methanol in water cm^2/s

D_{O_2W} is the molecular diffusivity of oxygen in water cm^2/s

N_{O_2} is aerator oxygen delivery rating (2 to 4 lb O_2/hr·hp)

E is aerator power delivery efficiency (0.65 to 0.90)

ω is the nameplate horsepower, hp

α is correction factor for wastewater/clean water oxygen transfer (0.8 to 0.85)

T is water temperature in ^oC

V is the volume of agitated water, ft^3

Freeman (1979) gives information from which reasonable values of A_t, a_v, and V can be obtained as a function of aerator horsepower, ω. TABLE 13 contains these parameters.

Reinhardt (1977) absorbed ammonia in aqueous sulfuric acid in order to measure the gas-phase mass-transfer coefficient associated with flat-blade surface agitators and he developed the correlation:

TABLE 13. TURBULENT AREAS AND VOLUMES FOR SURFACE AGITATORS*

ω, Motor Horsepower, hp	A_t, Turbulent Area, ft^2	Effective Depth, ft	V, Agitated Volume, ft^3	a_v, Area per Volume, ft^2/ft^3
5	177	10	1,767	0.100
7.5	201	10.	2,010	0.100
10	227	10.5	2,383	0.0952
15	284	11	3,119	.0909
20	346	11.5	3,983	.0870
25	415	12	4,986	.0833
30	491	12	5,890	.0833
40	661	13	8,587	.0769
50	855	14	11,970	.0714
60	1075	15	16,130	.0666
75	1452	16	23,240	.0625
100	2206	18	39,710	.0555

* This data is for a high speed (1200 rpm) aerator with 60cm propeller diameter.

$$N_{Sh} = 0.00039\ N_{Re}^{1.42}\ N_P^{0.40}\ N_{Sc}^{0.5} / N_{Fr}^{0.21} \qquad (32)$$

where: the Sherwood number, $N_{Sh} = k_g^t d/\rho_g D_{AA}$

the Reynolds number, $N_{Re} = d^2\omega/\nu_g$

the power number, $N_p = pg_c/\rho_l d^5\omega^3$

the Schmidt number, $N_{Sc} = \nu_g / D_{AA}$

the Froude number, $N_{Fr} = d\omega^2/g$

With dimensionless numbers any consistent set of units may be used and k_g^t is the gas-phase mass transfer coefficient, d is impeller diameter, ρ_g is the density of air, D_{AA} is the diffusivity of methanol in air, ω is the rotational speed of the impeller, radians/s, ν_g is the kinematic viscosity of air, P is the power to the impeller, g_c is the conversion factor 32.2 ft·lb mass/lb force·s^2, ρ_l is liquid density and g is the gravitational constant.

Cohen, Cocchio and Mackay (1978) volatilized toluene and benzene from a laboratory lake in a wind tunnel and propose the following equation for the liquid phase-mass-transfer coefficient:

$$k_l^n = 11.4\ R_e^{0.195} - 5 \qquad (33)$$

for $.11 < R_e \leq 102$, where k_l^n is in cm/hr and

$$R_e = 7.07E - 3Y_{10}\ V_{10}^{5/4} / \nu_g \exp(56.6/V_{10}^{1/4}) \qquad (34)$$

where : V_{10} is wind velocity in cm/s at height Y_{10} above the water in cm

ν_g is air kinematic viscosity in cm^2/s

If R_e is less than 0.11, $k_l^n = 2.4$ cm/hr should be used. Equation 33 should be multiplied by the square root of the benzene/methanol molecular weight ratio as a correction since it is benzene specific.

Harbeck (1962) measured the evaporation of water from lakes and Thibodeaux and Parker (1974) transformed the result for the gas-phase mass-tranfer coefficient

$$k_g^n = .03(\frac{D_{AA}}{D_{WA}})\ V_8/A^{0.05} \qquad (35)$$

where k_g^n is in lb mol/hr·ft^2, D_{WA} is the diffusivity of water vapor in air, V_8 is the wind velocity at 8 meters above the water surface in miles per hour, and A is the surface area of the water body in acres.

This completes the predictive model development.

MODEL PREDICTIONS OF METHANOL DESORPTION

During the field measurements using the CP technique sufficient environmenal data was obtained at the mill sites to provide the necessary input data for the predictive model. Due to the degree of variation encountered in environmental, chemical and physical parameters it was necessary to subdivide the eight sampling trips into ten categories for purposes of using the predictive model. The model was used for methanol. Although the measured acetone flux rates are reliable it was decided not to use acetone because the water chemistry was doubtful at the low concentrations encountered. TABLE 14 contains the environmental data and the concentrations of methanol in the water. TABLE 3 has basin operating data.

TABLE 15 contains the predicted flux rates, the corresponding CP technique measured flux rates and pertinent transport parameter results.

d. DISCUSSION OF PREDICTED VS. MEASURED FLUX RATES

As can be seen in TABLE 15 the range of the model predicted flux values are well within the range of those measured by the CP technique. Two interesting aspects of the model results can be inferred from a review of the transport parameters and the area calculations presented in the table. A review of the

TABLE 14. BASIN ENVIRONMENTAL AND METHANOL DATA

Mill Number:	1	1	1	2	2	3	3	4	4	4
Water Temperature (^{o}C)	25.3	28.7	28.7	28.4	33.6	34.3	36.4	35.8	35.1	35.1
Wind Speed (mi/h)	2.8	3.3	9.1	15.7	13.2	7.4	7.5	11.0	6.2	11.9
Air Temperature (^{o}C)	23.9	27.1	27.1	19.8	25.2	28.1	24.1	30.4	26.8	26.8
Conc. in H_2O (mg/l)	15.0	15.0	15.0	16.6	28.5	11.8	11.8	10.1	-	-
Henry's Constant *	.24	.30	.30	.28	.38	.39	.45	.43	.42	.42

* $y = Hx$

TABLE 15. PREDICTED FLUX VS MEASURED FLUX

Mill Number	1	1	1	2	2	3	3	4	4	4
Model Flux ($ng/cm^2 \cdot s$)	.37	.58	1.5	2.8	5.9	1.6	1.8	1.9	1.1	1.9
Measured ($ng/cm^2 \cdot s$)	.78	4.0	4.0	4.3	2.1	.62	.48	2.9	.47	.47
k_l^t ($lb\ mol/hr \cdot ft^2$)	953	1123	1123	1051	1283	342	366	1829	1768	1768
k_g^t ($lb\ mol/hr \cdot ft^2$)	1.07	1.07	1.07	1.18	1.18	.436	.435	.759	.758	.758
k_l^n ($lb\ mol/hr \cdot ft^2$)	2.40	2.40	0.570	1.22	.984	.384	.395	.765	2.40	.857
k_g^n ($lb\ mol/hr \cdot ft^2$)	.0397	.0506	0.140	.246	.231	.148	.155	.198	.109	.210
A_n (ft^2)	1.15E7	-	-	3.67E6	-	2.94E5	-	4.78E6	-	-
A_t (ft^2)	2.63E4	-	-	3.37E4	-	1.05E4	-	8.42E3	-	-

four mass transfer coefficients indicate that the gas-phase coefficient on the natural portions of the basin is controlling. This coefficient is the smaller of the four in all ten simulation cases. A comparison of the natural basin surface area values, A_n, and the aerator influenced surface area values, A_t, indicate that the natural dominates. This coupled with the fact that kg is the controlling coefficient suggest that the surface aerators are playing an insignificant role as chemical strippers.

The results of this study with methanol should not be interpreted to mean that the entire predictive model has been verified. More verification work is needed. Study should be made with chemicals that are liquid phase controlled. The influence of the aerators should be an important factor in this case.

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APPENDIX A

PUBLICATIONS RESULTING FROM THIS PROJECT

1. Heck, Howell H., "Theoretical Considerations of the Desorption of Organic Volatile Chemicals from an Aerated Stabilization Basin Treating Kraft Pulp and Papermill Wastewater", Unpublished M.S. Special Report, Civil Engineering, University of Arkansas, Fayetteville, Arkansas, 1978.

2. Dickerson, Richard L., "A Technique for the Measurement of Certain Wastewater Volatiles", Unpublished M.S. Thesis, Chemical Engineering, University of Arkansas, Fayetteville, Arkansas, 1980.

3, Thibodeaux, L.J. and Parker, D.G., "Emission of Volatile Chemicals from Wastewater Treatment Plants", Paper Presented at the Southern Regional Meeting of the National Council of the Paper Industry for Air and Stream Improvement, New Orleans, LA. 1979.

4. Heck, Howell H., Parker, D.G., Thibodeaux, L.J., and Dickerson, R.L., "Measurement of Volatile Chemical Emissions from Aerated Stabilization Basins", Paper to be Presented at National Conference on Environmental Engineering, ASCE, Atlanta, GA, July, 1981.

5. Thibodeaux, L.J., Parker, D.G., Heck, H.H., and Dickerson, R.L., "Quantifying Organic Emission Rates from Surface Impoundments with Micrometeorological and Concentration Profile Measurements", Paper No. 127a, 1981 Ann. Mtg. Amer. Inst. Chem. Eng., New Orleans, La., Nov. 8-12, 1981.

APPENDIX B

SAMPLE FIELD DATA*
(example)

Sample No. 2-1-3S CONCENTRATION PROFILE DATA Date of Sample 4/8/80

* Copies of the field data sheets are available from the Project Officer or authors.

Air Samples:

Velocity		Concentrations(ng/L)					Temperatures		
height (cm)	velocity (cm/s)	height (cm)	Meoh	Aceo	Acel	Thc	height (cm)	T_{dry} (°F)	T_{wet} (°F)
45.4	467	4.4	978	17.0		1085	0	83	83
65.4	506	12.7	817	14.1		869	7.6	67.3	56.7
105.4	557	22.9	721	17.6		813	15.2	66.0	55.8
185.4	648	55.9	492	15.6		552	30.5	67.1	57.8
265.4	694	88.9	430	15.7		490	76.7	64.7	52.7
345.4	723	175.3	424	-		445	7.6	65.8	55.5
							15.2	65.3	55.0
							139.7	65.1	49.7
							228.6	64.4	50.6

Water Samples:

Location	Concentration(mg/L)				Temperatures
	Meoh	Aceo	Acel	Thc	(°F)
#3	16.06	-	-	21.74	83

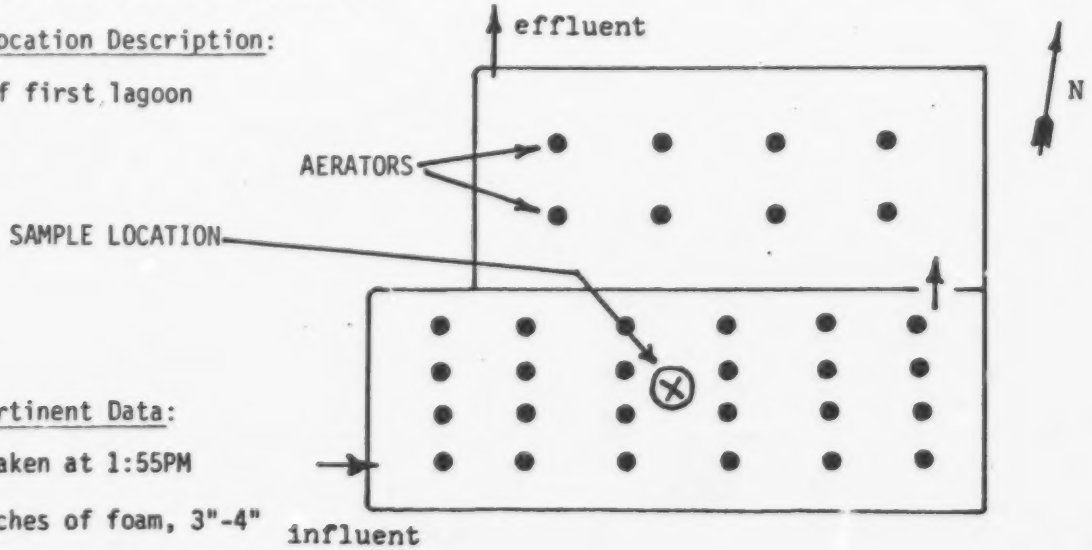
General Environmental Conditions:

Wind westerly

Surface partially covered with foam

Sample Location Description:

Middle of first lagoon



Other Pertinent Data:

Sample taken at 1:55PM

Some patches of foam, 3"-4" thick.

APPENDIX C

CORRECTING CONCENTRATION FOR T, P AND H

The effect of temperature, pressure and air humidity differences between the measurement point in the sample train and the sample point must be considered. FIGURE C1 shows a portion of the sample train and the locations of the measurement point "m" in sample point "s".

Air at temperature T_s and pressure p_s of humidity H_s containing the VOC is pulled in at point "s". The water vapor and VOC is condensed-frozen out in the u-tube trap. Upon reaching the measuring point "m", the pressure has been reduced to P_m, the temperature reduced to T_m and humidity to H_m, assumed zero.

Concentration, ρ_A (ng/l), of the VOC can be determined by:

$$\rho_{A1} = M_A/V_S \qquad (C1)$$

where M_A is the mass of species A collected in the trap for a time (6 minutes) and V_S is the volume of air at the sample point processed in this same period of time. Perry[1] gives the following equation for the volumetric flow rate through a rotameter

$$q_m = KD_f \sqrt{W_f (\rho_f - \rho_m) \rho_m/\rho_f \rho_m^2} \qquad (C2)$$

where q_m is the volumetric flow rate at the measuring point. ρ_f is the float density and ρ_m is the density of the air at "m". The float used had

[1]Perry, R. H., Chemical Engineers' Handbook, 4th Edition, pp. 5-22 (1977).

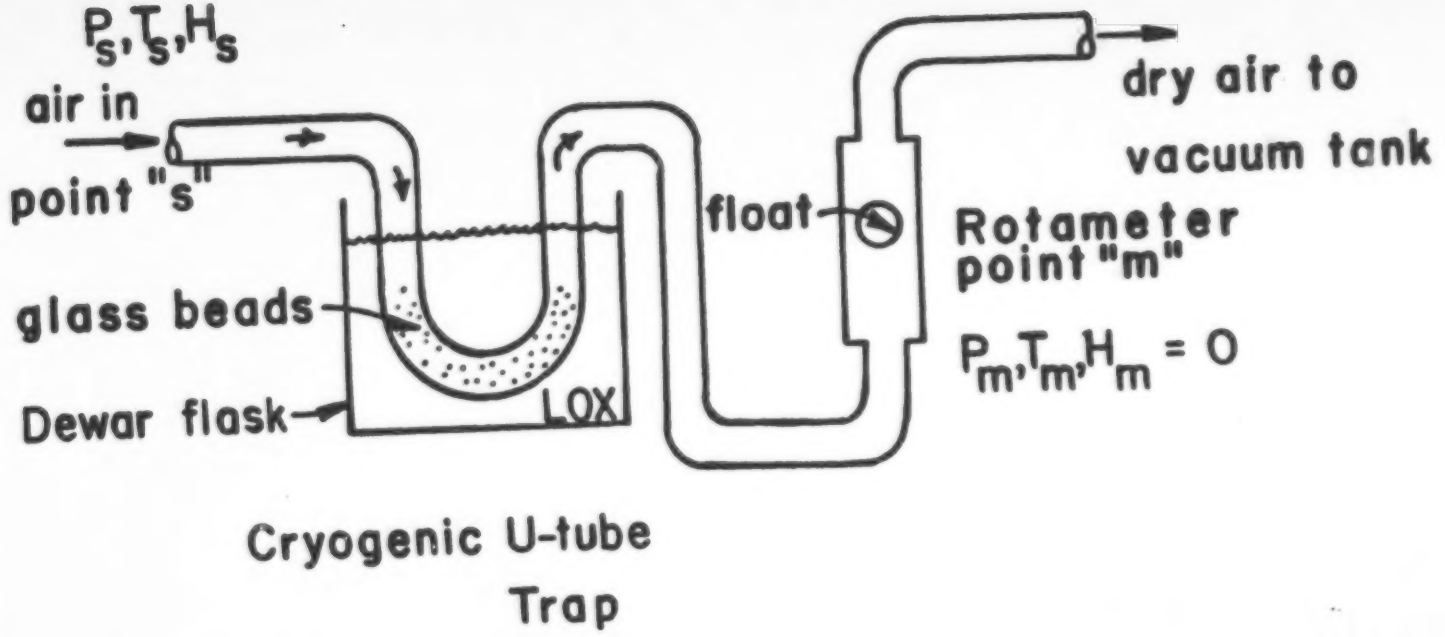


FIGURE C1. Cryogenic Sample Train

a weight of 0.0427 grams and a diameter of 3.2 mm for a density 0.311 g/cm^3. Dry air of STP has a density of 0.00120 g/cm^3, therefore $\rho_f >> \rho_m$ and Equation C2 simplifies to

$$q = KD_f \sqrt{W_f/\rho_m} \qquad (C3)$$

Using the ideal gas law and a sample time t yields

$$V_m = qt = KD_f t \sqrt{W_f RT_m/P_m M_m} \qquad (C4)$$

which is the volume measured. The volume sampled, V_s, can be obtained by using the conditions at point "s" (i.e., T_s, P_s, M_s) to create the ratio:

$$V_s = \sqrt{\frac{T_s}{T_m}\frac{P_m}{P_s}\frac{M_m}{M_s}}\ V_m \qquad (C5)$$

where the quantity under the radical is the change of state correction factor. If all the water vapor is assumed to be trapped in the u-tube, then the volume reaching the measure point will be reduced. The overall correction factor is then:

$$V_s = \sqrt{\frac{T_s}{T_m}\frac{P_m}{P_s}\frac{M_m}{M_s}}\ \frac{P_s}{P_m}\ V_m \qquad (C6)$$

where P_s and P_m are the total pressure with and without water vapor.

TABLE C1 shows typical pressures, temperatures and humidities observed and/or expected at "s" and "m".

Using the worst conditions of each variable the correction factor can be estimated from Equation C6 and is

$$\sqrt{\left(\frac{296.5}{276.5}\right)\left(\frac{731.9}{733.9}\right)\left(\frac{29.00}{28.96}\right)}\left(\frac{733.9}{733.9-2.2}\right) = 1.038$$

TABLE C1. Sample Train T, P and H

Parameter	Value at Measure Point	Value at Sample Point	Comment
P, mm Hg	732.9	733.9	Lab. air, 100 cc/min
P, mm Hg	732.3	733.9	Air 100% wet
P, mm Hg	732.3	733.9	Lab. air, 100 cc/min
P, mm Hg	731.9	733.9	Air 100% wet
T, ^{o}K	276.5	296.5	above at T_s=23.5^{o}C Air cooled 20^{o}C
P_{H_2O}, mm Hg	0.0	2.2	Sat. air at 40^{o}C
M_A (g/mol)	29.00	28.96	Sat. air at 40^{o}C

It appears that a typical worst case correction factor amounts to 3.8%. The air volume at the sample point will be slightly higher than at the rotameter. This means that a concentration computed with V_m instead of V_s will be high by no more than 3.8%.

APPENDIX D
SAMPLE CALCULATIONS

This appendix outlines the equations needed to determine the vertical flux rate of chemicals from a basin. First the necessary equations are presented and second the equations are used to calculate the flux rate from data collected in the field.

The vertical flux is defined as (4):

$$N_B = \frac{-k^2 S_\rho S_v (D_{Bl}/D_{Al})^{2/3}}{\phi_m^2 \; Sc_{Al}^{(t)}} \qquad \text{(Eq. D1)}$$

where: N_B = the vertical flux ($ng/cm^2.sec$)
k = the von Karman constant (.4)
S_ρ = the slope of the chemical concentration curve (ng/cm^3)
S_v = the slope of the wind velocity curve (cm/sec)

$(D_{Bl}/D_{Al})^{2/3}$ = the molecular diffusivity ratio, it corrects the turbulent diffusivity to the chemical in question from water

ϕ_m^2 = corrects for the diabatic velocity profile

$Sc_{Al}^{(t)}$ = the Schmidt number, it corrects for diabatic chemical concentration profiles.

The chemical concentration profile and the wind velocity profile are measured above the water surface. The slopes are defined as follows:

$$S_\rho = \frac{\rho_1 - \rho_2}{\ln y_1 - \ln y_2} \qquad \text{(Eq. D2)}$$

where: ρ_1 and ρ_2 are the chemical concentrations at height y_1 and y_2 respectively

y_1 and y_2 are the heights where the concentrations are known.

$$S_v = \frac{V_{x1} - V_{x2}}{\ln y_1 - \ln y_2} \qquad \text{(Eq. D3)}$$

where: V_{x1} and V_{x2} are the velocities at y_1 and y_2

To determine ϕ_m^2 and $Sc_{A1}^{(t)}$ the Richardson number has to be calculated.

The Richardson number is calculated as follows:

$$Ri \simeq \frac{g}{\bar{T}_1} \frac{(T_{12}-T_{11})(y_2 - y_1)}{(V_{x2}-V_{x1})^2} \qquad \text{(Eq. 44)}$$

where: g = the acceleration due to gravity (980.7 cm/sec^2)
$\bar{T}_1$ = the temperature at $\bar{y}$(^{0}K)
T_{12} = the temperature of air at height 2 (^{0}K)
T_{11} = the temperature of air at height 1 (^{0}K)
y_2 and y_1 = heights 2 and 1, respectively (cm)
V_{x1} = the wind velocity at height 1 in the horizontal direction (cm/sec)
V_{x2} = the wind velocity at height 2 in the horizontal direction (cm/sec)
$\bar{y}$ $= \left(\frac{y_1^2 + y_2^2}{2}\right)^{1/2}$

Knowing the Richardson number, the following correlation has been shown.

$$\frac{1}{\phi_m^2 \, Sc_{A1}^{(t)}} = (1- 50Ri)^{1/2} \quad \text{for unstable conditions (Ri is negative) in the range } |Ri| \leq 4 \qquad \text{(Eq. D5)}$$

$$= (1+ 50\ Ri)^{-1/2} \quad \text{for stable conditions (Ri is positive) in the range } |Ri| \leq 1 \qquad \text{(Eq. D6)}$$

$$= 1 \text{ for neutral conditions.}$$

These are all the equations needed to solve for the vertical flux. Using the data from Figure 7 the solution is as follows:

$$(D_{B1}/D_{A1})^{2/3} = \left(\frac{0.132}{0.220}\right)^{2/3} = 0.711$$

$$S_p = \frac{1000 - 400 \text{ ng/L}}{\ln 4.3 - \ln 155} = -167 \text{ ng/L}$$

$$S_v = \frac{450 \text{ cm/sec} - 650 \text{ cm/sec}}{\ln 43 - \ln 200} = 130 \text{ cm/sec}$$

$$Ri = \frac{980.7\ cm/sec^2(64.4 - 67.1^{\circ}F)(228.6 - 30.45\ cm)}{525.75\ ^{\circ}R\ (660\ cm/sec - 380\ cm/sec)^2} = -.014$$

Temp. data from field book is 64.4°F at 228.6 cm and

67.1°F at 30.45 cm

$$\frac{1}{\phi_m^2\ Sc_{Al}^{(t)}} = (1 - 50(-.014))^{\frac{1}{2}} = 1.30$$

$$N_B = .4^2(-167\ ng/L\ )(130\ cm/sec)(.711)(1.30)(\frac{1L}{1000\ cm^3})$$

$= 3.2\ ng/cm^2sec$

Which is the answer in TABLE 10 for sample 2-1-S3.